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ON THE ACTION OF ALKYL THIOCYANATES AND ALKYL ISOTHIOCYANATES WITH THIOL ACIDS.

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THE fact that dithiocarbamic esters are formed from alkyl thiocyanates and hydrogen sulphide led Chanlaroff[1] to examine the behavior of ethyl thiocyanate, C_2H_5SCN, with thioacetic acid, thioacetic anhydride, and thiobenzoic acid. He found, in each case, that the compounds reacted and that crystalline products resulted. However, he only described the addition product with thioacetic acid, and to this he assigned the formula $CH_3CONHCS.SC_2H_5$. He remarked, that this addition product behaved like a "molecular-verbindung" and that it showed such great instability in its reactions that all attempts to prepare a derivative from it, of any sort, were without success.

Numerous acyl dithiocarbamates of this type have been prepared by Dr. T. B. Johnson and ourselves, and we have found that derivatives can easily be prepared from the above and also from a large number of other acyldithiourethanes.

Our work has shown that thiocyanates, RSCN, readily react with thiol acids, on the steam-bath, in at least two ways. The

[1] *Ber. d. chem. Ges.*, **15**, 1987 [1882].

more commonly observed reaction is a direct addition as found by Chanlaroff:

$$\text{I. } C_2H_5SCN + HSCOC_6H_5 = C_2H_5S.CSHNCOC_6H_5.$$

Primary monothiocyanates, with aliphatic groups, as well as those prepared from benzyl, *p*-brom, *p*-nitrobenzyl, and *m*-xylyl halides, react almost entirely in this manner and very small amounts of by-product are formed. The di- and polythiocyanates appear to behave in a different manner and work on these is now in progress here.

Certain thiocyanates, even when the action is moderated by heating in the presence of benzene, react in a complicated manner. They evolve hydrogen cyanide and thiol esters result. The action apparently takes place in the following stages:

$$\text{II. } C_6H_5SCN + HS.COC_6H_5 = C_6H_5S.COC_6H_5 + HNCS.$$

The thiocyanic acid which is liberated then breaks down into hydrogen cyanide and other products.[1] Besides, it has been observed to react with thiobenzoic present in the following manner:

$$\text{III. } HNCS + HS.COC_6H_5 = H_2NCOC_6H_5 + CS_2.$$

The products are carbon disulphide and benzamide and the reaction is similar to that of hydrogen sulphide and thiocyanic acid when ammonia and carbon disulphide are obtained.[2]

In these latter reactions the products are, therefore, thiol esters, benzamide, hydrogen cyanide, and carbon disulphide; occasionally hydrogen sulphide is noticed, probably as a decomposition product of the thio acid, and in certain cases, especially when the reactions are performed without benzene, the above products are accompanied by thick oils, varnishes, or tars from which it is difficult to isolate anything solid in a state of purity.

The isothiocyanates, RNCS, or mustard oils react even more energetically with thio acids than the normal thiocyanates. When phenyl mustard oil or allyl mustard oil is warmed with thioacetic or thiobenzoic acid, a reaction takes place below the boiling-point of benzene, apparently in a quantitative manner as follows:[3]

$$\text{IV. } RNCS + HS.COC_6H_5 = RNHCOC_6H_5 + CS_2.$$

[1] Peter Klason: *J. prakt. Chem.*, [2], 26, 57 (1887).

[2] Voelckel: Pogg. *Ann.*, **65**, 313 (1845).

[3] Since the above was written Eibner (*Ber. d. chem. Ges.*, **34**, 660) has published the surprising statement that phenyl mustard oil does not react with thioacetic acid on long heating in a tube at 100°. We find that the substances react at ordinary temperature.

This reaction is of the same nature as that of thiocyanic acid with hydrogen sulphide, thiobenzoic acid, etc., mentioned above. It is also analogous to that observed by Kay,[1] who found that phenyl mustard oil and benzoic acid gave carbon oxysulphide and benzanilide, although at a much higher temperature than that in the present experiments.

Not only the alkyl, but also the acyl, isothiocyanates behave in this manner. Benzoyl rhodanide, C_6H_5CONCS, and thiobenzoic acid, for example, gave off carbon disulphide and dibenzamide was isolated and identified.

The above reactions sharply distinguish the thiocyanates from the isothiocyanates, and when a rhodanide is heated with thiobenzoic acid, the non-formation of carbon disulphide may be considered as conclusive proof that an isothiocyanate or mustard oil form is not present. We have now applied these reactions to the examination of some compounds described as mustard oils.

Before entering on the discussion of this it may be well to state that when reactive organic halogen compounds are boiled with potassium thiocyanate, the first product formed appears, in all cases, to be a normal thiocyanate, R—SCN. When the group R is strongly negative[2] the product immediately undergoes a molecular rearrangement into the form RNCS[3] (when R is the group C_6H_5CO—, etc.).

Less negative groups, such as the allyl group,

$$CH_2{=}CH{-}CH_2{-},$$

permit of the isolation of the primary product, allyl thiocyanate, if heating is avoided, otherwise allyl mustard oil is obtained. When, in other cases, a halide of the form $-CH_2X$ is employed the thiocyanates show the greatest stability. Methyl thiocyanate is only partially converted into mustard oil on heat-

[1] *Ber. d. chem. Ges.*, **26**, 2848 (1893).

[2] Miquel: *Ann. chim. phys.*, (5), **11**, 318 (1877); Dixon: *J. Chem. Soc.* (London), **75**, 388 (1899).

[3] The mechanism of this reaction or rearrangement appears to the writer to be as yet unexplained. The view accepted at present that the more negative the group, the more readily the rearrangement takes place (compare Michael: *J. prakt. Chem.*, **37**, 510 (1888), requires some modification, since data have already been collected that are not in accordance with this view. We hope to return to this subject at a later date. The methylene dissociation theory of Nef (*Ann. Chem.* (Liebig), 298, 370 (1897)) does not offer a simple explanation of the rearrangement which, in all probability, takes place in the case of acyl sulphocyanates. An attempt to prepare normal benzoyl thiocyanate, $C_6H_5CO.SCN$, by acting on potassium thiolbenzoate, suspended in benzene, with cyanogen bromide gave benzoyl disulphide as the chief product. W.

ing at a temperature of 180°–185°.[1] Recently, however, a number of cases have been described in which the grouping $-COCH_2X$ is said to yield mustard oils directly.

According to Beckurts[2] and Frerichs,[3] on carefully treating chloracetylethylurethane, $ClCH_2CONHCO_2C_2H_5$, with potassium thiocyanate, a mustard oil derivative is formed; namely,

$$SCNCH_2CONHCO_2C_2H_5.$$

The mustard oil structure was assigned to this from the fact that when the compound is treated with alkali and then with hydrochloric acid, hydrogen sulphide is evolved. When this substance is heated it undergoes a molecular rearrangement into what the above authors considered was the normal thiocyanic derivative, but later work showed that the rearranged product was a hydantoïn.[4]

The belief that iso- and normal thiocyanates resulted in this experiment led Frerichs and Beckurts[5] to examine rhodanacetic acid and its derivatives and they claim that none of the salts and esters described by Claësson have the normal form, but that all are derived from isothiocyanic acid. They add that rhodanacetamide prepared from chloracetamide also has the mustard oil structure.

In a later paper, Frerichs and Beckurts[6] state that no normal thiocyanacetic acid exists, and that there are no derivatives of the same. In other words, these compounds are all mustard oils, while according to their last paper[7] rhodanacetanilide has the normal form $NCSCH_2CONHC_6H_5$, and the perfectly analogous rhodanacetmethylanilidehas the iso structure $SCNCH_2CONCH_3C_6H_5$.

The fact that these compounds give off hydrogen sulphide under the above-named conditions is the only fact, as yet published, on which the iso or mustard oil structure is based. Since we have found that certain compounds of the normal form give off hydrogen sulphide under similar treatment, the beautifully crystallizable benzyl thiocyanate, $C_6H_5CH_2SCN$, for example, it is at once evident that this reaction cannot be used as a test for isothiocyanates.

We have, therefore, prepared and examined the behavior of all of

[1] Hofmann: *Ber. d. chem. Ges.*, **13**, 1350 (1880).
[2] *Arch. d. Pharm.*, **237**, 286.
[3] *Ibid.*, 237, 304 (1899).
[4] *Arch. d. Pharm.*, **238**, 319; *Centrlb.*, **71**, (2), 182 (1900).
[5] *Arch. d. Pharm.*, **238**, 9; *Centrlb.*, **71**, (1), 589 (1900).
[6] *Arch. d. Pharm.*, **238**, 320; *Centrlb.*, **71**, (2), 182 (1900).
[7] *Arch. d. Pharm.*, **238**, 615; *Centrlb.*, **71**, (2), 1270 (1900).

the above compounds as well as various analogues with thiobenzoic acid and our results show conclusively that not a single one of these rhodanides has the mustard oil structure. Not only the esters of Claësson have the formulas originally assigned to them, but also the homologous series of rhodanides, recently prepared in this laboratory, are true thiocyanates.[1]

This is shown by the fact that in the reactions with thiobenzoic acid, the substances combine to form addition products or acyl dithiourethanes. That not even a trace of a mustard oil is present in these compounds follows from the entire absence of carbon disulphide in the reactions.

As far as the authors are aware it has not been observed that the usual molecular rearrangement of thiocyanates into mustard oils is a reversible reaction. Even were this true, in view of the fact that the mustard oils react with thiol acids more readily than with the thiocyanates, the assumption that in these reactions the compounds undergo a rearrangement into normal forms is excluded.

The results, now at hand, show that *neither isothiocyanacetic acid nor any of its derivatives have yet been prepared.*

In Beilstein's Handbuch[2] the rhodanide which results on boiling 1,2-dichlorpropylene with potassium thiocyanate[3] is listed both under the heading of thiocyanates and of mustard oils. We find, when this product is warmed with thiobenzoic acid, that carbon disulphide is evolved in quantity and that 2-chlorpropylene benzamide, $CH_2=CCl—CH_2NHCOC_6H_6$, is formed. This rhodanide is therefore a mustard oil.

Berthelot[4] states, from thermochemical investigations,[4] that phenyl thiocyanate was observed to be transformed, for the greater part, into isothiocyanate on simply standing during a summer month. Our experiments with this substance do not confirm this statement. We have observed that it remains practically unaltered on keeping at a temperature of 34°–36° for four weeks. Perhaps these conflicting results are to be explained by the fact that, in certain cases, a small amount of foreign substance or impurity acts by catalysis and is capable of producing a molecular rear-

[1] Wheeler and Barnes: *Am. Chem. J.*, **24**, 60 (1900).
[2] Vol. I, 1279 and 1283.
[3] Henry: *Ber. d. chem. Ges.*, **5**, 188 (1872); *Bull. Soc. Chim.*, (Paris), **39**, 526 (1883).
[4] *Compt. rend.*, **132**, 57; *Ann. chim. phys.*, (7), **22**, 327 (1901).

rangement, as in the case of the imido esters and thioncarbamic esters, etc.

The statement of Chanlaroff in regard to the unstable nature of acetyl dithioethylcarbamate would indicate a wide difference between properties of acyl dithiocarbamates and the acyl thioncarbamates; we find, however, that the two series are closely similar in some respects, and that acylimidodithiocarbonic esters can be obtained from the sodium salts of these carbamates with no greater difficulty than attends the preparation of other imidothiocarbonic esters.[1] The reaction proceeds as follows:

V. $CH_3CO{-}N{=}C\begin{matrix}SNa\\SC_2H_5\end{matrix} + IC_2H_5 =$

$$CH_3CON{=}C\begin{matrix}SC_2H\\SC_2H_5\end{matrix} + NaI.$$

The lower members of this series as well as the corresponding benzoyl derivatives distil unaltered under diminished pressure. In a later paper the results of an examination of these compounds will be more fully given, especially those containing different alkyl groups, since, according to Hantzsch, they should exist in stereoisomeric forms. When these acylimidodithiocarbonic esters are treated with ammonia and organic bases a new type of pseudothioureas result. The reaction proceeds smoothly in the cold, with evolution of mercaptan as follows:

VI. $C_6H_5CON{=}C\begin{matrix}SCH_3\\SCH_3\end{matrix} + HNRR' =$

$$C_6H_5CON{=}C\begin{matrix}NRR'\\SCH_3\end{matrix} + HSCH_3.$$

Hitherto only one acylpseudothiourea has been obtained in a state of purity,[2] namely, monoacetylethylisodiphenylthiourea, $C_6H_5N = C(SC_2H_5)N(C_6H_5)COCH_3$; this, however, was prepared by a different method. It formed a thick oil which could not be crystallized. The compounds obtained by us differ most decidedly from the oxygen analogues and from the compound of Dains by their great tendency to crystallize and the ease with

[1] Liebermann: *Ann. Chem.* (Liebig), **207**, 141 (188); Fromm and Block: *Ber. d. chem. Ges.*, **32**, 2210 (1899); Busch and Lingenbrink: *Ibid.*, 2620; Wheeler, Barnes, Johnson, and Dustin: *Am. Chem. J.*, **24**, 60; *Ibid.*, 189; *Ibid.*, 424 (1900).

[2] Dains: This Journal, **24**, 197 (1900).

which they can be purified. A description of their reactions is reserved for a later paper.

As there appear to be no data in the literature in regard to the behavior of acyldithiocarbamic esters with organic bases we have investigated the action of aniline on some of the acetyl and benzoyl derivatives. It was shown in a previous paper[1] that the acylthioncarbamic esters react in an abnormal manner with ammonia and aniline, that hydrogen sulphide was evolved and pseudoureas were formed. An analogous reaction appears to take place with the dithio esters and aniline; inasmuch as hydrogen sulphide is evolved, however, by far the chief products are normal ureas, the behavior being more strictly analogous to that of acetylurethane which was thoroughly investigated by Young and Clark.[2] As a contribution to our knowledge of the saponification of urethanes by aniline we examined also the behavior of benzoylethylcarbamate, $C_6H_5CONHCO_2C_2H_5$. We were unable to detect any signs of the formation of a pseudourea in this case; the chief reaction took place with the formation of benzoylphenylurea and alcohol.

As found by Chanlaroff, ammonia acts on the acyldithiocarbamic esters of the above type; with complete decomposition, mercaptan and ammonium thiocyanate are formed. This reaction is in marked contrast with that of the acylthioncarbamic esters, $C_6H_5CONHCS.OC_2H_5$, for example, which with alcoholic ammonia in the cold, passes quantitatively into benzoylpseudoethylurea,

$$C_6H_5CON=C\begin{matrix}NH_2\\ \diagup\\ \diagdown\\ OC_2H_5\end{matrix}.$$

In this connection it is interesting to note that the "imidodicarbonsäuretrithiodibenzyl ester," $C_7H_7S.CONHCS.SC_7H_7$, prepared from phenylmethyldithiomonobenzyldi-*c*-methylketuret and concentrated hydrochloric acid, according to Fromm and Junius,[3] reacts in the normal manner since monothiobiuret and benzyl mercaptan are formed. We find that a similar normal reaction takes place with the acylthiolcarbamic esters, mercaptan is evolved, and an acylurea is obtained. These three reactions with ammonia are apparently peculiar to the different series of acyl thiocarbamates.

[1] *Am. Chem. J.*, **24**, 189 (1900).
[2] *J. Chem. Soc.* (London), **73**, 361 (1898).
[3] *Ber. d. chem. Ges.*, **28**, 1105 (1895).

EXPERIMENTAL PART.

The thiocyanates are capable of combining or reacting with thioacetic and thiobenzoic acid at a much lower temperature than that at which Chanlaroff worked. In all cases a smoother reaction is brought about by simply warming a few hours in benzene solution. In certain cases the substances combine at ordinary temperature after long standing. The acyldithiocarbamates thus formed, are all soluble in alkali and most of them can be purified (from disulphide) by precipitating with carbon dioxide. They are converted by a 10 per cent. sodium hydroxide solution, as a rule, into colorless plates of the sodium salts which dissolve on further dilution. The action of alkali, however, produces more or less decomposition into rhodanide and mercaptan, with the formation of thiobenzoic and hydrocyanic salts. They are almost all readily soluble in hot alcohol, but with difficulty in cold, and, like urethanes in general, they form beautiful crystals. They have a yellow color without exception.

Acetyldithiomethyl carbamate, $CH_3CO.NHCS.SCH_3$, is formed practically quantitatively when the constituents are heated dry, or with benzene as a solvent. When crystallized from alcohol it forms long, slender, bright yellow prisms which melt at 119°. A nitrogen determination gave:

	Calculated for $C_4H_7ONS_2$.	Found.
Nitrogen.....	9.3	9.2

Acetyldithioethyl carbamate is the only one of these carbamates that has hitherto been described. It is formed at ordinary temperatures when the rhodanide and thioacetic acid are allowed to stand for a number of weeks, or almost quantitatively when heated for a short time on the water-bath. It forms long, bright yellow prisms which melt at 123°.

Acetyldithiodiethyl carbonate, $CH_3CON=C\begin{matrix}SC_2H_5\\SC_2H_5\end{matrix}$.—When 22 grams of the above carbamate, 3.1 grams of sodium, dissolved in 125 cc. of alcohol, and 20 grams of ethyl bromide were mixed, a reaction took place in a short time and sodium bromide separated. After standing a number of hours, water was added and the precipitated oil was extracted with ether, washed, dried, and distilled at 14 mm. pressure, whereupon 19.2 grams of colorless oil

were obtained, boiling sharply at 142° (74 per cent. of the calculated). There was no sign of decomposition during the distillation and an analysis of this oil gave :

	Calculated for $C_7H_{13}ONS_2$.	Found.
Nitrogen.....	7.3	7.6

When this compound is treated with organic bases mercaptan is evolved and pseudothioureas are formed.

Acetyldithionormalpropylcarbamate, $CH_3CONHCS.SC_3H_7$, was prepared from normal propyl rhodanide, boiling at 164° at 761 mm. pressure. This combines smoothly with thioacetic acid and the product crystallizes from dilute alcohol in brilliant yellow plates or flattened prisms melting at 78°. A nitrogen determination gave :

	Calculated for $C_6H_{11}ONS_2$.	Found.
Nitrogen.....	7.9	7.7

Cetyl thiocyanate, $C_{16}H_{32}SCN$.—Kahlbaum's cetyl iodide (30 grams) readily reacted with potassium thiocyanate in alcoholic solution. The product boiled at 242°–249° at 30 mm. pressure, and at 222° to 227° at 13 mm. pressure. It forms a colorless liquid which, on cooling, solidifies to a white wax. The latter portion of the above distillate, when solidified, showed signs of melting at 12° and then melted at 15°–15.5°. A nitrogen determination gave :

	Calculated for $C_{17}H_{33}NS$.	Found.
Nitrogen.....	4.94	4.88

Acetylcetyldithiocarbamate, $CH_3CONHCS.SC_{16}H_{33}$.—The above thiocyanate readily combined with thioacetic acid, on warming three or four hours on the steam-bath. It then solidified to a yellow cake of fine radiating crystals. On crystallizing from alcohol it formed a bulky mass of fine hair-like needles which had a lighter yellow color than the lower members of the series, and which melted at 89°–90°. The material dissolved completely in very dilute alkali ; in moderately dilute, it was converted into a mass of colorless, very thin plates of the sodium salt. An analysis gave :

	Calculated for $C_{19}H_{17}ONS_2$.	Found.
Nitrogen.....	4.13	4.43

Acetyldithiobenzylcarbamate, $CH_3CONHCS.SCH_2C_6H_5$, was

smoothly formed from its constituents. It crystallized from alcohol in bright yellow plates melting at 136°, and a nitrogen determination gave :

	Calculated for $C_{10}H_{11}ONS_2$.	Found.
Nitrogen.....	6.22	6.50

Benzoyldithiomethylcarbamate, $C_6H_5CONHCS.SCH_3$, is smoothly and apparently quantitatively formed when methyl rhodanide and thiobenzoic acid are warmed for a short time. It forms long, slender, yellow needles melting at 135°, and a nitrogen determination gave :

	Calculated for $C_9H_9ONS_2$.	Found.
Nitrogen.....	6.63	6.34

Benzoyldithioethylcarbamate, $C_6H_5CONHCS.SC_2H_5$, is formed as readily as the methyl derivative. It crystallizes from alcohol in stout, yellow prisms melting at 84°. The determination of nitrogen was as follows :

	Calculated for $C_{10}H_{11}ONS_2$.	Found.
Nitrogen.....	6.22	6.22

Benzoyldithiodimethylcarbamate, $C_6H_5CON=C\begin{matrix}SCH_3\\SCH_3\end{matrix}$.—Twenty grams of benzoyldithiomethylcarbamate were added to a solution of 2.2 grams of sodium, in methyl alcohol, and then 20 grams of methyl iodide. The mixture, on standing a number of hours, was precipitated with water and the product extracted with ether. On evaporating the ether, after drying, long colorless prisms separated which after crystallizing from dilute alcohol melted at 46°. Yield about 15 grams.

	Calculated for $C_{10}H_{11}ONS_2$.	Found.
Nitrogen.....	6.22	6.26

Benzoyldithiodiethylcarbamate, prepared in a similar manner to the above, proved to be an oil, boiling at 220°–221° at 17 mm. pressure. Ten grams of the urethane gave about 6 grams of the oil, and, on analysis, the following per cent. of nitrogen was obtained :

	Calculated for $C_{12}H_{15}CONS_2$.	Found.
Nitrogen.....	5.53	5.88

Benzoylpseudomethylthiourea, $C_6H_5CO-N=C\begin{matrix}NH_2\\SCH_3\end{matrix}$. — When 4.7 grams of benzoyldithiodimethyl carbamate were dissolved in an excess of alcoholic ammonia and allowed to stand for two days, mercaptan separated, and, on evaporating the alcohol and crystallizing the residue from a mixture of benzene and ligroin, about 2 or 3 grams of material melting at 111°–112° were obtained. A nitrogen determination gave:

	Calculated for $C_9H_{10}ON_2S$.	Found.
Nitrogen	14.43	14.53

Benzoylpseudomethylphenylthiourea, $C_6H_5CON=C\begin{matrix}NHC_6H_5\\SCH_3\end{matrix}$, was prepared by warming the above dimethyl carbamate, on the water-bath, with aniline. It forms thin colorless plates from alcohol, which melt at 104°–105°.

	Calculated for $C_{15}H_{14}ON_2S$.	Found.
Nitrogen	10.37	10.57

Benzoylpseudoethylphenylthiourea, prepared from the above diethyl carbamate by warming with aniline, formed long colorless prisms from alcohol which melted at 87°–88°.

	Calculated for $C_{16}H_{16}ON_2S$.	Found.
Nitrogen	9.85	9.84

Benzoyldithionormalpropylcarbamate, $C_6H_5CONHCS.SC_3H_7$, is formed as readily as the above dithioethyl carbamate. It crystallizes in bright yellow prisms from alcohol, and it melts at 77°. A nitrogen determination gave:

	Calculated for $C_{11}H_{13}ONS_2$.	Found.
Nitrogen	5.85	5.81

Benzoyldithioisobutylcarbamate, $C_6H_5CONHCS.SC_4H_9$. — This forms transparent golden yellow needles, some over an inch in length, when prepared from isobutylthiocyanate boiling at 178°–180°. It melts at 80°–81°, and an analysis gave:

	Calculated for $C_{12}H_{15}ONS_2$.	Found.
Nitrogen	5.53	5.53

Benzoyldithiocetylcarbamate, $C_6H_5CONHCS.SC_{16}H_{33}$, was

formed as smoothly as its lower homologues. It forms a beautiful mass of shining, bright yellow plates, when crystallized from alcohol, and it melts at 63°–64°. A nitrogen determination gave:

	Calculated for $C_{24}H_{39}ONS_2$.	Found.
Nitrogen.....	3.32	3.30

Benzyl Thiocyanate, $C_6H_5CH_2SCN$.—The melting-point of this compound is given by Henry[1] as 36°–38°, and by Barbaglia[2] as 41°. A portion prepared from benzyl chloride and potassium thiocyanate was crystallized several times from absolute alcohol; it then melted at 43°–43.5°. A portion of this was treated with dilute sodium hydroxide, and on adding acid then, after warming, or on letting the material stand, hydrogen sulphide was given off. This was easily recognized by its odor and the black color it gave with lead acetate paper.

Benzoyldithiobenzylcarbamate, $C_6H_5CONHCS.SCH_2C_6H_5$, results smoothly when the constituents are warmed in benzene solution. No hydrogen cyanide or carbon disulphide is formed in this case. When crystallized from alcohol it forms long yellow needles melting sharply at 108°. A nitrogen determination gave:

	Calculated for $C_{15}H_{13}ONS_2$.	Found.
Nitrogen.....	4.87	4.92

This compound gives a difficultly soluble sodium salt which separates from aqueous alkali in colorless, thin plates. It is readily soluble in alcohol and it is one of the most stable salts of this series, although warm alkali rapidly decomposes it.

Phenyl Thiocyanate, C_6H_5SCN, *and Thiobenzoic Acid.*—The thiocyanate, in this case, was freshly prepared by the method of Gattermann and Hausknecht.[3] It was allowed to digest, on the water-bath, with thiobenzoic acid for two or three days, whereupon, on cooling, a mass of crystals separated. This material contained no nitrogen and it proved to be identical with *phenyl thiolbenzoate*, $C_6H_5CO.SC_6H_5$, described by Schiller and Otto,[4] and which melts at 56°.

A portion of this thiocyanate (7.8 grams) was allowed to stand at 34°–36° for twenty-eight days, whereupon it was heated with thiobenzoic acid in benzene (20 cc.) for two hours and a

[1] *Ber. d. chem. Ges.*, **2**, 637 (1869).
[2] *Ibid.*, **5**, 689 (1872).
[3] *Ibid.*, **23**, 739 (1890).
[4] *Ibid.*, **9**, 1635 (1876).

half. The benzene was then distilled off and found to contain some hydrogen cyanide and a small amount of carbon disulphide. On cooling, nothing solid was obtained, and no solid was separated by adding ether (absence of notable quantities of benzanilide). In fact, it was found that a large portion of the rhodanide had remained unaltered in this treatment. Unaltered thiobenzoic acid was removed by alkali, and on evaporating the ether solution, nothing but phenyl thiolbenzoate was obtained. The quantity of benzanilide, if formed at all, was insignificant. These results show that phenyl thiocyanate does not readily undergo a molecular rearrangement into phenyl mustard oil, although Berthelot states, from the results of his thermochemical investigations[1] that the thiocyanate was transformed, for the greater part, on simply standing during a summer month.

2, 4-Dinitrophenyl Thiocyanate, $C_6H_3(NO_2)_2SCN$, *and Thioacetic Acid*, when heated together, gave a product insoluble in ether, benzene, and alcohol. From nitrobenzene it crystallized in small yellow pyramids which had no definite melting-point; at 250° it began to decompose and was not completely melted at 280°. It was insoluble in alkali. Although a nitrogen determination agreed with the calculated for a dithiocarbamate, the properties of the substance, however, show that this is *tetranitrophenyldisulphide*, $(C_6H_3(NO_2)_2S—)_2$, which has been described by Willgerodt.[2] The nitrogen determination was as follows:

	Calculated for $(C_6H_3(NO_2)_2S—)_2 = C_{12}H_6O_8N_4S_2$.	Found.
Nitrogen	14.0	14.2

When this substance is heated on platinum it explodes.

2, 4-Dinitrophenyl Thiocyanate and Thiobenzoic Acid were heated together on the water-bath without benzene. A violent evolution of gas took place which was allowed to pass through water; this then responded to the Prussian-blue test for hydrogen cyanide but gave no test for thiocyanic acid. On crystallizing the residue from 95 per cent. alcohol, plates were obtained which melted at about 100°. This material proved to be impure *benzoyldinitrothiophenol*, which is said to melt at 113° (Willgerodt) or at 111°.[3] On treating this with alkali and then adding acid, the above-mentioned *tetranitrophenyldisulphide* was obtained.

[1] *Loc. cit.*

[2] Beilstein's "Handbuch," **2**, 816; compare *Ber. d. chem. Ges.*, **9**, 978, and **10**, 1686 (1877).

[3] Kym: *Ber. d. chem. Ges.*, **32**, 3532 (1899).

Rhodanacetylethylurethane and Thiobenzoic Acid.—If rhodanacetylethylurethane has a mustard oil structure it should act with thiobenzoic acid with the formation of hippurylurethane and carbon disulphide. Instead of this, the action took an entirely different course. 5.7 grams of the rhodanide, prepared according to the directions of Frerichs, and melting at 86°, were dissolved in 45 cc. of benzene, and 4.2 grams of thiobenzoic acid were added. The mixture was heated on the water-bath for eight hours, with a return condenser, whereupon a portion of the benzene was distilled off and tested for carbon disulphide, by adding an alcoholic solution of potassium hydroxide. No precipitate of potassium xanthate was obtained, and on adding copper sulphate solution no yellow precipitate resulted. The reaction product was therefore free from carbon disulphide. The alkaline solution gave the Prussian blue test for hydrogen cyanide. The benzene solution was filtered from a small amount of material and, on cooling, minute yellow crystals separated. These formed the chief product of the reaction. When these were crystallized from alcohol thin, golden yellow plates were obtained, which melted at 159°. The color and the following analysis show that this substance is *benzoyldithiocarbamicacetylethylurethane*,

$$C_6H_5CONHCS.SCH_2CONHCO_2C_2H_5:$$

	Calculated for $C_{13}H_{14}O_4N_2S_2$.	Found.
Nitrogen.....	8.58	8.50

Rhodanacetylethylurethane, therefore, has the structure

$$NCS.CH_2CONHCO_2C_2H_5.$$

Rhodanmethyl Acetate and Thiobenzoic Acid.—The action of the thiocyanic esters of acetic acid with thiol acids is well represented by rhodanmethyl acetate. The behavior of this alone is described here since that of others as well as certain homologues have been used in other work and will be described in a later paper. When the rhodanide in question was warmed with thiobenzoic acid no carbon disulphide resulted and no methyl hippurate was obtained. Thirteen grams of thiobenzoic acid and 12 grams of rhodanmethyl acetate were diluted with 30 cc. of benzene and heated to boiling for six hours. On evaporating off the benzene and crystallizing from alcohol, 14 grams of bright yellow prisms melting at 118° were easily obtained. The properties of the substance and the following nitro-

gen determination show that this is *benzoyldithiocarbamicmethyl acetate*, $C_6H_5CONHCS.SCH_2CO_2CH_3$:

	Calculated for $C_{11}H_{11}O_3NS_2$.	Found.
Nitrogen.....	5.24	5.65

In the process of formation of the above, traces of hydrogen cyanide are evolved, but otherwise, there appears to be very little by-products formed. It follows, therefore, that rhodanmethyl acetate is a derivative of normal thiocyanic acid and not a mustard oil.

Rhodanacetamide and Thiobenzoic acid, on heating together in benzene solution, evolved hydrogen cyanide and on cooling benzoyldisulphide separated in quantity. On distilling off the benzene and testing for carbon disulphide none was found. This fact establishes that rhodanacetamide is not a mustard oil. The remaining material in the benzene solution was not obtained in a state of purity. It formed a black tar.

Benzoylthioglycollamide, $C_6H_5COSCH_2CONH_2$.—This was prepared from potassium thiolbenzoate and chloracetamide, in order to compare it with the products in the above experiment. It crystallizes from hot water in long colorless prisms which melt at 119°–120°. A nitrogen determination gave:

	Calculated for $C_9H_9O_2NS$.	Found.
Nitrogen.....	7.18	7.35

Rhodanacetmethylanilide and Thiobenzoic Acid.—When 6.6 grams of this rhodanide and 4.4 grams of thiobenzoic acid with 35 cc. benzene were heated for five hours on the water-bath, no carbon disulphide was formed and nothing corresponding to hippurmethylanilide was obtained. The Prussian blue test showed the presence of hydrogen cyanide and on evaporating off the benzene a tar was found. On treating this with ether and on crystallizing the solid which separated from dilute alcohol yellow, flattened prisms or tables were obtained, which melted at 152° (0.2–0.3 gram). A nitrogen determination agreed with the calculated for *benzoyldithiocarbamicmethylacetanilide*,

$C_6H_5CONHCS.SCH_2CON(CH_3)C_6H_5$:

	Calculated for $C_{17}H_{16}O_2N_2S_2$.	Found.
Nitrogen.....	8.13	8.08

The above results show that rhodanacetmethylanilide is a derivative of normal and not isothiocyanic acid.

Allyl Isothiocyanate, C_3H_5NCS, *and Thiobenzoic Acid* react immediately on gently warming, carbon disulphide streams off and the remaining light yellow colored oil distils almost entirely from 175°–176° at 14 mm. pressure. Kay[1] gives the boiling-point of *allylbenzamide* as 173°–174° at 14 mm. pressure. The carbon disulphide evolved in these reactions is pure and it has no disagreeable odor, but suggests somewhat that of ether. That it is carbon disulphide was shown in each case by the xanthate test.

Phenyl Isothiocyanate, C_6H_5NCS, *and Thiobenzoic Acid* reacted very readily on the steam-bath; carbon disulphide was evolved and the residue solidified. On crystallizing from alcohol large plates of *benzanilide* melting at 161° were obtained.

Phenyl Isothiocyanate and Thioacetic Acid on standing at ordinary temperatures for a month deposited a mass of colorless plates of acetanilide melting at 114°.

α-Chlorallyl Isothiocyanate, $CH_2=CCl—CH_2NCS$, *and Thiobenzoic Acid.*—The isothiocyanate was prepared according to the directions of Henry and 5 grams of this were heated with 5.2 grams of thiobenzoic acid in 45 cc. of benzene. After six hours a portion of the benzene was distilled off and this gave an abundant precipitate of xanthate with alcoholic potassium hydroxide. No hydrogen cyanide could be detected. The reaction product was boiled with water to remove some oil and then crystallized from a mixture of benzene and petroleum ether whereupon it was obtained in long colorless flattened prisms melting at 95°. A nitrogen determination agreed with the calculated for *2-chlorallylbenzamide*, $C_6H_5CONHCH_2—CCl=CH_2$:

	Calculated for $C_{10}H_{10}NCl$.	Found.
Nitrogen.....	7.17	7.31

Benzoyl Rhodanide, C_6H_5CONCS, *and Thiobenzoic Acid* were warmed for a short time on the water-bath, carbon disulphide was given off, and the residue was treated with alkali and ether (to remove some benzonitrile). The alkaline solution on acidifying gave a product which, on crystallizing from dilute alcohol, formed needles melting at 148°. This material was, therefore, *dibenzamide.*

[1] *Loc. cit.*

Ethyl Selenocyanide, C_2H_5SeCN.—This compound, which appears to be new, was prepared from 16.1 grams of potassium selenocyanide and 15 grams of ethyl bromide in alcohol solution. The reaction is complete in a few minutes, and it is best then to add water without distilling off the alcohol. The oil is somewhat volatile in alcohol vapor and also in that of ether. On distilling at 741 mm. pressure it practically all boiled at 172°. It formed a pale yellow oil with a highly disagreeable odor. A nitrogen determination gave:

	Calculated for C_3H_5NSe.	Found.
Nitrogen.....	10.44	10.38

When this was warmed with thiobenzoic acid it gave off a gas or vapor, with the odor of hydrogen cyanide, and an oil and a solid were obtained. These products were not investigated.

AN IMPROVED METHOD FOR THE RAPID ESTIMATION OF SUGAR IN BEETS.

By R. S. Hiltner and R. W. Thatcher.

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INTRODUCTION.

EXPERIENCE has abundantly shown that both the good and the bad properties of any individual beet are largely hereditary and may be transmitted to succeeding generations of beets. The success of the beet-sugar industry in recent times has been due to a very large extent to the building up of a race of high-grade beets by means of the selection of individual beets having high sugar content for the production of the seed for later use. Long-continued and careful efforts in this direction have resulted in the production of beets of highly satisfactory sugar-producing qualities. This condition is more or less abnormal, however, and the tendency is toward a retrogression or reversion to the original state. In order to prevent this and to maintain the present high state of perfection, constant care in the selection of only the best beets for mothers for seed production is necessary. Not only is it essential to select those beets which possess the best form of leaves and root, but care must also be taken that only those whose roots are of high sugar content are used. The sugar content of individual beet roots under the same conditions of growth varies

widely. It is obvious, therefore, that a knowledge of the sugar content of each beet which is selected is of the utmost importance. The necessity of some simple, rapid, and accurate method for testing small samples taken from individual beets is therefore apparent. Moreover, the rapid development of the beet sugar industry in this country of late, emphasizes the need of some such rapid method adapted to factory control.

DISCUSSION OF PRESENT METHODS.

Many of the methods already suggested for the determination of sugar in beets are very satisfactory as far as accuracy is concerned, but all are more or less complicated and require the use of expensive apparatus and great care in manipulation. Furthermore, a large force of laboratory assistants is necessary in order to make the process of any of the known methods of analysis rapid enough for control work in the selection of mother beets. Dr. François Sachs, of Brussels, Belgium, in a paper read before the second International Congress of Applied Chemistry held in Paris, July 27 to August 5, 1896, gives a very clear and concise statement of the present methods for the analysis of sugar beets and suggests certain modifications and improvements in them. Inasmuch as this article has not yet appeared in American chemical literature, we quote the more pertinent portions of it below:[1]

"We may divide the methods which have been proposed, for this purpose, into three groups:

"1. The indirect methods based upon the analysis of the juice.

"2. The alcoholic methods.

"3. The aqueous methods.

"The indirect methods no longer have any more than an historic interest, and their use, particularly in France, is gradually disappearing, more rational methods taking their place.

"It has long been believed that the use of alcohol is indispensable for the exact determination of the percentage of sugar contained in the beets. Even to-day this appears to be the opinion held by most German sugar chemists. In fact, when one removes the pulp of the sugar beet, extracts with alcohol, and washes the exhausted pulp with water, the aqueous solution thus obtained turns a ray of polarized light distinctly to the right. Hence, it has been concluded that alcohol is necessary to perfect

[1] Translation made by Division of Chemistry, Department of Agriculture, Washington, D. C.

the solution of optically active bodies, such as sugar. But it has been demonstrated, notably by the work of two Belgian chemists, Chevron and Droixhe, that the precipitation of these active bodies (which appear to be pectic bodies) is complete when subacetate of lead is added to their aqueous solution.

"It is necessary to conclude, after what has been said, that the alcohol and aqueous methods ought to give the same results with the same beets. This is exactly what has been observed by Pellet, Petermann, Weisberg, and others. The objection has been made that Petermann did not obtain in all of his experiments absolutely identical results, but the differences are so small that they may well be attributed to errors in sampling. Moreover, subsequent experiments made with greater care have given results still more concordant. It may seem that the results obtained by the aqueous diffusion method are too high by about 0.1 per cent., because the hydration of the marc is not taken into account, but this same error must occur when the alcoholic diffusion methods are used.

"On the other hand, the results obtained by the cold aqueous diffusion methods may be too high if the analyst neglects to completely eliminate the air imprisoned in the fine pulp, as has been frequently observed, notably by Woijcki in Russia, and by Nassou at Gembloux. When all of the common errors are eliminated, in the application of the two methods, no sensible difference between the results have been observed, either in Belgium or in France. In Germany, on the contrary, most of the chemists generally continue to affirm that the alcoholic methods give more exact results than the aqueous methods, and that for certain abnormal beets the differences may be very considerable.

"I shall not stop to discuss the hot aqueous diffusion methods which give good results, but which have not the desired simplicity. The cold aqueous diffusion, designed by our colleague, M. Pellet, is much more practical. However, as has already been said, this method as it is generally applied requires the complete elimination of the air imprisoned in the pulp, and therefore demands especial care. Moreover, the introduction of the pulp by means of a funnel into a flask with a more or less narrow neck, is an operation which it is very desirable to dispense with.

"It is these considerations that led us to modify the ordinaryl methods by introducing the pulp into a large ungraduated vesse

and adding to it at once by means of a pipette, the proper quantity of lead subacetate and water. This method was announced two years ago (April 24, 1894) at the meeting of the Association of Belgian Chemists. We then incorrectly attributed the original idea to Woijcki. We wish to say now that it should be credited to Kaiser and Lewenberg.

"Kaiser[1] proposed to use 26.048 grams of the finely rasped pulp with the addition of 76 cc. of water and lead subacetate solution. He used a special correction in the case of very rich beets.

"Lewenberg[2] directed the use of 26.048 grams of the finely rasped pulp, 3 cc. of lead subacetate and 73.8 cc. of water.

"Woijicki[3] designed a simple apparatus, by means of which he demonstrated that in the ordinary method even as much as 3.1 cc. of air is left in the flask.

"Walawski[4] proposed to take any convenient weighed quantity of the beet pulp and to add to it 3.6 times its weight of water and lead subacetate solution. This modification does not appear to us to be a desirable one.

"We have in our turn simplified somewhat the form of the apparatus used. We have found it convenient to use for the normal weight, 26.048 grams of the beet pulp, about 5 cc. of lead subacetate solution, and a sufficient quantity of water to bring the total volume of the liquid contained in the pipette to 77 cc. We tried this method and the results were not satisfactory. We found that it was necessary to shake the mixture for a very long time in order to obtain a complete distribution of the sugar throughout. We then decided to modify the method more radically and for that purpose constructed a pipette, having a capacity of 177 cc., which enabled us to obtain the conditions recommended for the ordinary method. Working in this manner we obtained perfectly satisfactory results. We have never found that more than three minutes are necessary to obtain a complete distribution of the sugar throughout the mixture."

OBJECTIONS TO PRESENT METHODS.

Any of the methods now in use will give fairly accurate and

[1] *Deutsche Zuckerindustrie*, 1893, p. 413.
[2] Dodatek, 1892.
[3] *Gazeta Cukrowiczna*, 1893, p. 313; *Oester. Zeitschrift*, 1894, p. 146.
[4] *Gazeta Cukrowiczna*, 1894, p. 268; *Oester. Zeitschrift*, 1895, p. 1117.

satisfactory results if carefully carried out. They all possess in general, however, certain inherent sources of error, the inaccuracies resulting from which become greater and greater as carefulness of manipulation is sacrificed to speed. The several sources of error which may be mentioned here are as follows: First, the pulp itself is susceptible to changes in composition during weighing, both through the evaporation of its water and through pressure exerted by the appliances used in transferring the pulp from the dish containing it to the weighing capsule. In rapid work, where pincers or some similar appliance must be used to transfer small portions of the pulp either to or from the weighing dish in order to obtain the exact normal weight, the change in composition of the pulp thus handled becomes quite significant. Moreover, as in all cases where only a portion of the sample is used for analysis (the normal weight or some fraction or multiple thereof), unless great care is taken the portion which is weighed out does not accurately represent an average of the whole sample. Second, the amount of lead subacetate to be used in clarifying the juice varies, and too much or too little of the reagent is liable to be added, with a resulting effect upon the polarization value of the solution. Third, the sample of pulp occupies some space in the flask and the flask does not, therefore, contain exactly 100 cc. of liquid (*i. e.*, sugar solution). This error is compensated for in most cases by using flasks which are graduated at 101.3 cc., the 1.3 cc. additional being adopted as the average value for the volume occupied by the pulp. This requires, of course, specially constructed flasks, and the figure thus arbitrarily adopted is more or less far from the truth in individual cases. Fifth, as has been noted in the article quoted above, the pulp mechanically encloses considerable air, and the error due to the change in volume of solution thus produced may in some cases become very significant. Finally, the volume to which the solution is made is always measured in graduated flasks, the calibration of which is not always accurately done.

Moreover, in all the present methods of analysis as employed in this country, there are certain steps in the process which require considerable care and the manipulation of which requires much time. These interfere seriously with rapid work, and the speed of the operation is consequently quite limited. In the first place, a certain definite weight of pulp must be obtained. If

this is done with a tolerable degree of exactness considerable time is consumed. Next, the pulp must be transferred to a flask having a somewhat narrow neck. Owing to the tendency of the particles of pulp to agglomerate, this is a difficult and tedious operation at best. In the third place, the volume of the solution must be made up to the mark on the neck of the flask with care. Since all aqueous solutions of beet juice froth badly while the water is being added, some precaution to break this froth is generally necessary and it is with difficulty that the process is carried out quickly.

An ideal method for the rapid determination of sugar in samples of beet pulp would, therefore, be one in which the entire sample as received from the drill would be used, the pulp itself would not be transferred from the dish into which it is first received, and the proportion of lead subacetate to the amount of pulp used would be constant. The article quoted above describes the recent attempts by European chemists to modify Pellet's method in order to conform more closely to these conditions. The modifications suggested obviate some of the objectionable features of the original method, but give more or less unsatisfactory results. In order to ascertain and to eliminate, if possible, the sources of error in the methods suggested by Dr. Sachs, and in order to take advantage of the more desirable features of these methods, the present work was undertaken.

THE PROPOSED METHOD. THEORETICAL CONSIDERATIONS.

In the following discussion the factors required by the Schmidt and Haensch polariscope are used exclusively. The principles involved are general, however, and the method of analysis may be used with any other make of instrument, the factors being changed accordingly.

It is evident that, in order that the scale of the instrument shall correctly show the percentage of sugar in the sample taken, a certain relation of weight of pulp taken to volume of solution must always be maintained; namely, 26.048 : 100. It is not necessary that the weight taken shall always be 26.048 grams. It may be any fraction or any multiple of this, but the volume of solution must be correspondingly decreased or increased, and the flask in which the solution is made up to volume must be calibrated accordingly. Hence, all methods of analysis now

in use require that the weight of pulp to be taken shall be some simple multiple or fraction of the normal weight, in order that the required volume may be 200 cc., 100 cc., or 50 cc., these being the volumes at which flasks are usually graduated. The 100 cc. of liquid in the solution required by the normal weight of pulp is made up of two components, namely, the water originally present in the juice of the sample and the water added to complete the proper volume. If, now, the quantity of water in the pulp be known, the residual quantity which must be added to give the correct volume of solution, can easily be determined. This amount of water may then be added directly to the pulp in the containing vessel and the necessity for transferring the pulp to a graduated flask and adding water to the mark be obviated. Furthermore, there would then be no necessity for taking just the normal weight of pulp or an even multiple or fraction thereof, since it is only necessary to preserve the ratio of weight to volume mentioned (that is, 26.048 : 100 or 1 gram : 3.839 cc.) in order to preserve the conditions required by the polariscope. In other words, any weight of pulp might be taken and sufficient water added to complete the volume of the solution in cubic centimeters to 3.839 times the weight of the pulp taken.

Not all beets contain the same percentage of water. It is a well-known fact, however, that in general this percentage does not vary through very wide limits. In most cases as the percentage of sugar in the beet increases the percentage of non-sugars decreases, or in other words the total solid matter in the beet does not change as rapidly as does the sugar content. A long series of determinations made at this Station during several years shows that for beets of from 8 per cent. to 15 per cent. sugar content the water content almost always falls between 80 per cent. and 84.5 per cent. Since such wide limits of sugar content, as those mentioned, would include most beets to be analyzed during any season or during a particular period of analysis, it would be possible to assume an average factor for water content which would vary from the true amount of water in any individual beet by not more than 2 per cent., except in very rare cases. A simple calculation will show that this maximum of error in the water factor will not change the dilution of the sugar solution sufficiently to cause a perceptible difference in the polariscopic reading. For example, 2 per cent. of 26.048 equals 0.52.

An error of 2 per cent. in the assumed water factor would then result in the addition of 0.52 gram, or cubic centimeters of water too much or too little. The resulting volume will therefore be 100 ± 0.52 cc., or it will be increased or decreased by 0.52 per cent. of itself, and the polariscopic reading will be correspondingly affected. A beet which should give a polariscopic reading of 14 will therefore read 0.52 per cent. of 14, or 0.07, too high or too low, an error scarcely appreciable in any ordinary polariscope. If in exceptional cases the error in the water factor should rise to 4 per cent. or even to 5 per cent., the corresponding error in the polariscopic reading would amount to less than 0.2 per cent., or in other words an extraordinarily poor beet having an unusually high percentage of water will give a reading slightly too low, or an exceptionally good beet may give a reading slightly too high, but in no possible case would the error due to this cause amount to more than 0.2. In analyses for the selection of mother beets it is customary to double the dilution in order to obtain a larger filtrate from a small sample of pulp, and then double the polariscopic reading. In case this should be done, the possible error due to variation of water content from the factor assumed would be diminished one-half, and in no possible case could there be an error amounting to 0.1 from this source.

It is possible, then, to assume a factor for the water content which will represent the true amount of water present in the beet so closely as to produce no appreciable error in the polariscope reading. If we represent this factor by x, the ratio of weight of pulp taken to the volume of water necessary to be added in order to bring the total volume up to the proper amount would be represented by $26.048 : 100 - 26.048\,x$. Having assumed, then, a value for x, this ratio may readily be calculated, and a table arranged to show the exact volume of water to be added to any given weight of pulp in order to bring the total water of the mass up to the correct volume for that weight. For example, if we assume 82 per cent. as this factor, the formula would then become $26.048 : 100 - (26.048 \times 0.82)$, or $26.048 : 78.64$, or $1 : 3.019$. Upon this basis, then, the volume of water to be added in any particular case would be 3.019 times the weight of pulp taken. A table could then be prepared showing the amount of water to be added for any particular weight of pulp taken. In case the samples are to be obtained by means of a boring rasp,

as recommended below, this table would not need to extend over more than 10 grams, between the limits of 5 and 15 grams, since all the samples obtained by the boring rasp will usually fall between these limits of weight. The following arrangement of the table has been found to be very satisfactory :

Grams.→	5	6	7	8	9	10 etc.
↓	cc.	cc.	cc.	cc.	cc.	cc.
0.00	15.10	18.12	21.14	24.16	27.18	30.20
0.02	15.16	18.18	21.20	24.22	27.24	30.26
0.04	15.22	18.24	21.26	24.28	27.30	30.32
0.06	15.28	18.30	21.32	24.34	27.36	30.38
0.08	15.34	18.36	21.38	24.40	27.42	30.44
0.10	15.40	18.42	21.44	24.46	27.48	30.50
etc.						

Such a table will show at a glance the desired volume to be added. For example, 5 grams of pulp would require the addition of 15.10 cc. of water ; 9.08 grams would require 27.42 cc., etc.

DETERMINATION OF AVERAGE WATER CONTENT.

For the purpose of obtaining figures from which to decide upon the number to be assumed as the water factor in calculating the quantity of water to be added to the pulp, a direct determination by taking samples from as many beets as possible should be made. The beets taken for this purpose should be of as widely different character and grown under as different conditions as are those which are subsequently to be analyzed by this process. A convenient method for determining the water content is as follows : The beet should be split in half longitudinally, and thin slices cut from one of the exposed surfaces from various parts of the beet until about 15 grams are obtained. These thin slices should be received on a weighed watch-glass or other similar dish, covered to prevent evaporation, and their weight immediately determined. The watch-glass should then be placed in a water oven and dried until the loss in weight in one hour is not more than 5 milligrams. From the total loss in weight the percentage of water originally contained may be calculated.

A simple determination of the total solid matter in the juice of the beet by the ordinary method, using a Brix spindle and calculating this value back to that for the original beet by means of the usual coefficient for marc, will not suffice if an accurate

result be required. Variations in the relative amounts of insoluble solids (marc) are too great. Furthermore, the fact that the Brix spindle is calibrated in solutions of pure sugar gives rise to an error which has been found to amount to as much as 1½ per cent. in some cases, and its reading is nearly always from 0.5 to 0.8 higher than the figure obtained by a direct determination of the total solids in the juice.

During the investigations upon the applicability of the proposed method made at this laboratory this season, the actual water content of some sixty beets was determined. These beets were taken from fields in five different sections of the state, and from each field beets of widely different appearance were selected. The following table shows the results of these determinations :

TABLE I. WATER CONTENT OF BEETS.

Sugar in beet. Per cent.	Number of analyses.	Water content. Maximum. Per cent.	Minimum. Per cent.	Average. Per cent.
8 to 10	11	86.04	82.72	84.64
10 to 12	30	85.22	80.56	83.05
12 to 14	13	83.63	79.91	82.10
Above 14	1	....	....	81.25
Not determined	6	85.16	80.54	82.69
	Total, 61			Average, 82.74

That the above results represent closely the normal condition of beets for any year and that the water content, to a very striking degree, is independent of the season, of weather, and of the kind of cultivation, is shown in the following table. These data were compiled from results obtained at the Nebraska Experiment Station. Excepting for the year 1898, the samples analyzed were taken from fields on the Station farm. Each year the beets were grown in a different field. The character of the soil in these fields differs considerably. Moreover the meteorological records for these successive years show a decided lack of uniformity in climatic conditions. The figures given for 1898 represent the composition of mature beets grown that year at Ames, Nebraska, where the character of the soil, the rain-fall, etc., are wholly different from that at Lincoln.

TABLE II.

Year.	No. of analyses.	Sugar in beet. Max.	Min.	Average.	Percentage of water. Max.	Min.	Average.
1892	9	14.2	10.8	12.7	83.70	80.75	81.74
1894	7	13.8	10.6	11.9	83.66	80.24	82.00
1895	9	10.3	7.3	8.6	85.64	83.64	84.51
1896	5	13.5	11.1	11.8	84.14	82.11	83.27
1897	10	13.8	10.8	12.3	83.65	80.26	81.89
1898	9	15.5	11.8	13.6	82.98	79.33	81.21

In spite of this diversity of conditions that affect the growth and development of the beet, the differences in the percentages of water contained are not large, as the above table shows. The grand average is 82.43 per cent. The largest percentage observed was 85.64, and the smallest, 79.33. The former was from an abnormally poor beet with a sugar percentage of 7.5 while the latter was from a high-grade beet containing 14.1 per cent. sugar. With these two exceptions the range of values is from 80.24 per cent. to 84.51 per cent.

All of these figures indicate that for beets, most of which contain between 8 per cent. and 14 per cent. of sugar, 83 per cent. might be assumed as an average water factor without there being a variation in any individual case of more than 3 per cent. As has been shown above, this variation will not produce an error of more than 0.1 in the polariscope reading. In a more favorable season, or portion of a season, when the beets average better, the average water content would be lower. For use in analysis of beets which have from 12 per cent. to 16 per cent. of sugar, the factor 82 per cent. or 81.5 per cent. would probably be found to be more nearly correct. In case unusually good beets are to be analyzed, for example, beets that have previously been carefully sorted out for use as mother beets for seed production, a still lower factor—80 per cent. or 78 per cent., depending upon the richness of the beets—would be selected.

From the above discussion it will be seen that the addition to the pulp of 3.6 times its weight of water and lead subacetate solution suggested by Walawski is erroneous and would give rise to grave inaccuracies. For example, 3.6 times the normal weight (26.048) equals 93.8. 100 cc. minus 93.8 cc. equals 6.4 cc., the water presumed to be present in the beet pulp. Since 6.4 cc. or grams of water is only 25 per cent. of the weight of the sample taken, the error in the supposition is apparent.

In the same way Kaiser's proposition to add 76 cc. of water and lead subacetate solution to the normal weight of pulp would yield erroneous results, since in this case it is supposed that 24 cc. (or approximately 92 per cent. of water) is present in the beet pulp, an unknown condition. Lewenberg's modification, increasing the volume of water and lead subacetate to be added to 76.8 cc., supposes the presence of 23.2 cc., or 89.2 per cent. of water in the beet pulp. This percentage of water is still much higher than that obtained by direct determination, and would introduce a corresponding error.

Dr. Sachs' method requires the addition of 77 cc. of water and lead subacetate solution to the normal weight. In this case allowance is made for 23 cc., or 88.3 per cent. of water, in the beet pulp. This high water factor may be the source of the unsatisfactory results which he first obtained and which he attributed to incomplete diffusion of the sugar present. The experience and observation of many analysts show that the diffusion of sugar is perfect and practically instantaneous, if the pulp is sufficiently fine, when only the ordinary or normal dilution is made. This makes unnecessary the double dilution of the solution (with its attendant increase of error in the polariscopic reading) as proposed by Dr. Sachs. The error due to the incorrect value for the water coefficient would of course be diminished one-half by the double dilution, and this possibly explains the more satisfactory results that were obtained thereby.

THE PROPOSED METHOD. DETAILS OF MANIPULATION.

This being a method depending upon cold aqueous diffusion of the sugar in the beet, it is absolutely essential that the sample to be analyzed, be reduced to an impalpable pulp in order that the diffusion of the sugar throughout the solvent may be complete. The boring rasp devised by Messrs. Kiel & Dollé has been found to be well adapted for this purpose.

The sample of pulp, after being rasped to a sufficient degree of fineness, is received directly into a tared capsule of the form suggested by Le Docte[1] and the weight of the pulp ascertained. For this purpose a balance which is sensitive to one centigram is sufficiently accurate, since it is not necessary to know the weight with more exactness than the nearest centigram. The process

[1] Spencer's "Handbook for Chemists of Beet-Sugar Houses", page 181.

of weighing may be facilitated by the use of a gram rider on the beam of the balance, in place of the usual fractional weights.

As soon as the weight of the pulp is ascertained, the volume of water to be added to this weight is read off from the table previously prepared as indicated above. Since the solution must be clarified as well as made up to definite volume, the water to be added should contain sufficient lead subacetate to clarify the mixture. For this purpose, water containing 3 per cent. by volume of a solution of lead subacetate of 54.3° Brix, or specific gravity 1.257, has been recommended and has been found to give excellent results. If it be desired to use acetic acid as recommended by Pellet, this may also be added to the water. For rapid work, the solution thus prepared should be contained in a reservoir connected with a burette having a two-way connection, which will automatically fill to the zero mark. The capsule containing the pulp is then held under this automatic burette and the volume of liquid which was ascertained from the table is discharged into the capsule. A quarter turn of the stop-cock, or proper adjustment of the pinch-cocks, closes the discharge and connects the burette with the reservoir so that it may fill to the zero, ready for the next sample.

The capsule containing the pulp thus properly diluted is then covered with a light disc of wood or glass, inclosed in a sheet of rubber so that it will fit closely to the top of the capsule and make a water-tight covering. The capsule is then grasped between the thumbs and forefingers in such a way as to press the cover down closely, and shaken vigorously. The sugar is diffused uniformly throughout the solution, practically instantaneously if the sample has been properly prepared. The cover may be coated with vaseline before use, and if slipped to one side, not lifted, in removing, it is in readiness for another determination.

The mixture is then poured on a dry filter and the remainder of the operation carried out as usual. The use of the Pellet continuous-flow observation tube materially shortens the time required for the polariscopic reading.

EXPERIMENTAL WORK.

The method thus described was used in the analysis of some sixty beets in this laboratory last fall. In every case a large sample of pulp from each beet was obtained, thoroughly

mixed to insure uniformity of composition, and then divided, one portion being analyzed by the new method and the other by the Pellet hot aqueous diffusion method—using double the normal weight of pulp and making the volume up to 202.6 cc. The beets were selected from the five different fields mentioned above, and the results obtained show that they varied in composition through wide limits. The water factor assumed in preparing the table for the analyses was 82 per cent. The beets did not prove to be so rich in sugar content as was expected, however, and the factor 83 per cent. would probably have represented more closely the average water content of the beets analyzed. This latter figure would probably have reduced somewhat the error in the results obtained for the very low-grade beets. The results of the analyses are shown in the following table:

TABLE III.—COMPARATIVE RESULTS OBTAINED BY THE NEW METHOD.

No.	Pulp taken. Grams.	Water added. cc.	Sugar by new method. Per cent.	Sugar by hot diffusion. Per cent.	Extent. of error.
1	17.33	52.34	6.2	6.25	— 0.05
2	7.61	22.95	13.6	13.7	— 0.1
3	23.34	70.50	11.9	11.9	..
4	11.88	35.88	13.1	13.05	+ 0.05
5	16.79	50.70	11.45	11.3	+ 0.15
6	12.27	37.06	11.85	11.85	..
7	25.08	75.74	5.5	5.9	— 0.4
8	18.60	56.17	10.1	10.2	— 0.1
9	23.37	70.57	10.8	10.7	+ 0.1
10	19.79	59.75	8.9	8.9	..
11	13.54	40.89	12.55	12.55	..
12	25.07	75.70	11.4	11.45	— 0.05
13	13.96	42.20	14.05	14.05	..
14	16.30	49.23	12.2	12.3	— 0.1
15	9.94	30.85	11.45	11.5	..
16	23.70	71.57	12.2	12.15	+ 0.05
17	22.79	68.80	10.0	9.95	+ 0.05
18	11.98	36.18	8.4	8.7	— 0.3
19	12.55	37.89	7.9	7.9	..
20	18.25	55.10	8.55	8.7	— 0.15
21	24.89	75.14	12.35	12.4	— 0.05
22	24.82	74.96	11.45	11.4	+ 0.05
23	17.78	53.68	10.0	9.95	+ 0.05
24	14.13	42.67	12.5	12.6	— 0.1
25	13.12	39.62	6.5	6.7	— 0.2
26	17.59	53.12	11.0	10.9	+ 0.1

No.	Pulp taken. Grams.	Water added. cc.	Sugar by new method. Per cent.	Sugar by hot diffusion. Per cent.	Extent of error.
27	21.85	66.00	10.0	9.9	+ 0.1
28	19.80	59.80	11.1	11.1	..
29	24.12	72.84	11.4	11.4	..
30	17.02	51.04	12.0	12.1	— 0.1
31	11.11	33.58	11.1	11.2	— 0.1
32	23.71	71.57	13.5	13.5	..
33	23.73	71.72	12.5	12.6	— 0.1
34	23.26	70.55	12.5	12.5	..
35	23.33	70.46	9.35	9.4	— 0.05
36	24.02	72.54	10.8	10.8	..
37	22.23	67.15	9.35	9.5	— 0.15
38	24.56	74.17	6.9	7.2	— 0.3
39	16.91	51.07	11.9	11.9	..
40	15.78	47.65	10.55	10.5	— 0.05
41	16.90	51.04	10.0	9.85	+ 0.15
42	18.32	55.33	12.45	12.55	— 0.1
43	26.04	78.64	10.5	10.5	..
44	20.00	60.40	10.4	10.45	— 0.05
45	13.96	42.16	11.6	11.6	..
46	16.18	48.86	11.85	11.9	— 0.05
47	17.07	51.56	10.95	11.1	— 0.15
48	15.21	45.93	7.1	7.05	+ 0.05
49	16.19	48.90	10.8	10.9	— 0.1
50	25.28	76.35	12.95	13.0	— 0.05
51	19.96	60.28	10.4	10.35	+ 0.05
52	20.00	60.40	11.0	11.0	..
53	13.56	40.95	9.9	9.8	+ 0.1
54	14.72	44.45	8.6	8.6	..
55	13.92	42.04	11.5	11.4	+ 0.1
56	18.52	55.93	8.0	8.2	— 0.2

Of these results only five (Nos. 7, 18, 20, 27, and 56) show a variation from those obtained by the hot aqueous diffusion, greater than might be obtained from duplicate samples analyzed by the same method. The five beets which gave results too low by 0.2 per cent., or more, are all very low-grade beets from which low results might be expected owing to the increased dilution of the solution to be polarized, because of the unusual amount of water present in the beets. It is generally admitted that the hot aqueous diffusion method of analysis gives scientifically accurate results if properly carried out. Since the new method gives results which compare so favorably with those obtained by this process, its accuracy and the fact that it is based on correct principles are established.

APPLICATION OF THE METHOD TO THE ANALYSIS OF MOTHER BEETS.

The principles of the method as outlined above permit the use of certain modified forms of the apparatus employed which will decrease to a very considerable extent the time required for making a single analysis and hence increase the number of analyses which may be made in a day. The most important of these modifications are described below.

Balance—For very rapid work, an automatic and self-registering balance, to be used in determining the weight of the sample of pulp, is very desirable. The new form of balance recently put upon the market by Kaehler and Martini would serve very well for this purpose, since the weight of any substance placed upon the pan of the balance is indicated on the dial face directly without the use of weights. With such a balance, all the weighings necessary for 1,200 or 1,500 analyses per day could probably be made by two assistants, one to wipe the capsules and place them on the balance pan, and the other to read and record the weights on the slips accompanying the samples. In the absence of such a balance an ordinary chemical balance of the heavier forms, sensitive to one centigram, may be used. The use of a one-gram rider on the beam in the place of the ordinary fractional weights will facilitate the weighing.

Capsules.—When large numbers of samples are to be analyzed in a very short time, the capsules into which the sample is received must all be of the same weight or tare. This can be attained by using metal capsules with a small button of tin or solder attached to the side or bottom. By filing or scratching this soft button, the weight of the capsule can be changed at will, and an equal tare for the entire set be obtained. Aluminum is a very desirable metal to be used for the construction of these capsules, since it affords the necessary rigidity and at the same time the very desirable feature of light weight. Capsules of this material are practically indestructible and are subject to only very slight changes in weight. They should be so constructed as to have a capacity of about 100 cc., and should weigh 25 to 30 grams. A shape similar to that of the ordinary porcelain crucible has been found to be a very satisfactory one for these capsules. They may, however, be made with straight walls and a

flat bottom with rounded corners.[1] The edge, upon which the cover is to be placed in agitating the contents, should be ground flat and may be reinforced by a ring of thicker metal if sufficient rigidity cannot be obtained otherwise. An equal number of lids which will fit the capsules fairly closely should be provided, in order that the pulp may be protected from evaporation during the time which elapses between the boring of the beet and the weighing of the sample. The lid should be removed at the instant the capsule is set on the balance pan, so that the prearranged tare may not be disturbed. When 1,000 to 1,500 analyses per day are to be made, at least 100 of these capsules should be provided.

Burette.—A 100 cc. burette, preferably one graduated in tenths of cubic centimeters, should be used. One graduated in fifths may be employed, but more care in reading is then necessary. The burette should be provided with an overflow at the zero mark[2] so that it will fill automatically to that point when connected with the reservoir containing the solution to be added. The manner of using the burette has been indicated in describing the details of the method. When used in this way, any desired volume of liquid can be quickly and accurately discharged.

The other apparatus necessary is identical with that required by any other method of analysis. A complete list of such apparatus has been published in Bulletin No. 60 of the Nebraska Experiment Station. The details of the method of obtaining the sample and of labeling the beet have been thoroughly discussed in the same bulletin.

THE ANALYTICAL OPERATION.

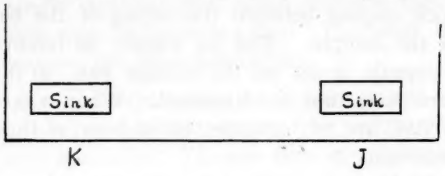
The details of the analytical operations may best be understood by reference to the following figure, which represents a laboratory table equipped for this work. This table should be about 14 feet in length and 3 feet in width. This size of table will permit independent action on the part of the operators, and at the same time avoid the necessity of any movement from one place to another.

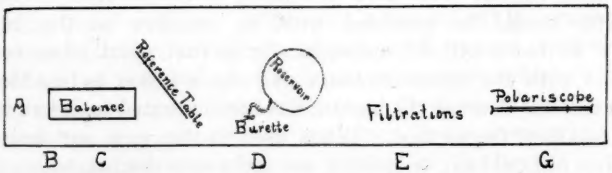
The capsules containing the samples of pulp are brought from the drill and placed on a table at A. The first assistant, stationed at B, takes one of the capsules, wipes off the outside, removes the

[1] See design in Spencer's "Hand-book for Chemists of Beet-Sugar Houses", p. 181.

[2] A burette similar to that offered by Kaehler and Martini (Catalogue No. 2170) has proved to be satisfactory for this purpose.

lid, and places the capsule on the pan of the balance. The weigher C notes the weight indicated by the balance. From the reference table at his right, he ascertains the volume of water to be added to this weight of pulp and records this on the slip accompanying the sample. He then passes the capsule and its slip on to his right. In the meantime, B has prepared another





capsule and placed it on the balance pan. The operator at D then takes the weighed capsule, reads from the slip accompanying it the volume to be added, places the capsule under the automatic burette, and adds this volume of liquid. The same turn of the stop-cock which closes the discharge connects the burette with the reservoir and it is immediately filled, ready for the next sample. The capsule is at once passed on to the assistant at E, who covers it with the rubber cap, agitates it vigorously for a few seconds, and then pours the contents on a filter, which has been placed in a stemless funnel in proper position in a sugar beaker by the wash-boy stationed at J. The empty capsule is then passed across the table to the wash-boy at K, who cleans it, ready to be returned to the drill for another sample. After the filtration is complete, the assistent at G pours the filtrate into the funnel of the observation tube of the polariscope, places the accompanying slip before the observer, and passes the funnel and beaker across the table to the wash-boy at J. The latter cleans and dries them and prepares them for repeated use. The observer adjusts the polariscope, and while he is reading the scale and

recording the result on the slip before him, a new solution is poured into the observation tube by the assistant at G.

The process is thus continuous and is susceptible of great speed of manipulation. In case the ordinary form of balance is used instead of the automatic balance, a larger number of balances and assistants to operate them is, of course, necessary. By making the table wider, another row of operators might be stationed on the opposite side, thus doubling the working capacity without greatly increasing the laboratory space necessary. Care should be exercised that sufficient space for the sinks and for the wash-boys is always provided, however, since the proper cleansing and drying of the apparatus is of extreme importance.

APPLICATION OF THE NEW METHOD TO INDIRECT OR JUICE ANALYSES.

Despite the statement quoted above, that the indirect method of analysis is regarded as having "only an historic interest" it is still in very general use in this country as a means of determining the value, or purchase price, of sugar beets as they are delivered at the factories. It affords a convenient as well as fairly rapid and fairly accurate method of determining the average sugar content and purity coefficient of a composite sample consisting of quite a large number of beets of varying composition.

Several methods of obtaining a definite weight or definite volume of juice for analysis are in general use. In each of them the tendency of the somewhat viscous juice to retain bubbles of air, bits of pulp, etc., introduces more or less of inconvenience or error. The most accurate method for obtaining the desired weight of juice is by direct weighing, the so-called "gravimetric method." The same objections which were mentioned in connection with the discussion of the process of obtaining a definite weight of beet pulp are equally applicable to this procedure. It was deemed desirable, therefore, to test the accuracy of the new method when applied to the analysis of the juice of the beet.

For the purpose of calculating the volume of water and lead subacetate solution to be added, a water factor of 85 per cent. was adopted. Eight beets of different physical appearance were selected, and the juice from each obtained in the usual manner. The juice was thoroughly mixed to insure uniformity; one sample of 26.048 grams was weighed out and analyzed by the

"gravimetric method," a second sample was measured in a sucrose pipette and the analysis completed as usual, and a third sample was analyzed by the new method. The results obtained are shown in the following table :

TABLE IV.—COMPARISON OF METHODS OF INDIRECT ANALYSIS.

Juice taken. Grams.	Liquid added. cc.	Sugar by new method. Per cent.	Sugar by gravimetric method. Per cent.	Sugar by pipette method. Per cent.
21.78	65.12	9.75	9.8	9.8
29.92	89.46	12.8	12.8	12.65
22.04	65.97[1]	6.35	6.4	6.3
20.02	59.84	10.9	10.9	..
28.36	84.50	9.35	9.35	9.35
23.91	71.49	10.95	11.0	10.95
25.00	74.75	11.10	11.15	11.05
25.13	75.14	13.55	13.65	13.60

These few results are sufficient to show that the new method is applicable to indirect analysis. In point of accuracy it does not possess any great advantage over the sucrose pipette method if the latter is carefully carried out. It has the advantage that no specially constructed apparatus is necessary and it requires slightly less time for its manipulation than do any of the other methods.

UNIVERSITY OF NEBRASKA, LINCOLN, NEBRASKA,
February 9, 1901.

[CONTRIBUTION FROM THE NORTH CAROLINA AGRICULTURAL EXPERIMENT STATION.]

THE RATE OF NITRIFICATION OF SOME FERTILIZERS.

BY W. A. WITHERS AND G. S. FRAPS.

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THE value of any fertilizer depends on its availability to the plant, that is, the readiness with which it can be absorbed directly by the plant, or converted into forms which can be assimilated. Nitrogen can be assimilated by plants directly in four forms; *viz.*—(1) free nitrogen; (2) as certain organic compounds; (3) as ammonium salts; (4) as nitrates.

Free nitrogen can be assimilated from the air by a class of plants with the aid of organisms living in nodules on their roots. This method of assimilation is confined to the leguminosae, which includes clover, peas, beans, the peanut, vetch, etc.

[1] Used water factor 90 per cent. in calculation.

Some organic compounds, such as urea, glycocoll, leucin, tyrosin, asparagin and acetamide, may be taken up directly by plants, and serve to nourish them. All of these compounds may occur in the soil. Urea is found in urine, asparagin in plants, and asparagin and tyrosin are often produced by the decay of animal or vegetable matter in the soil. All nitrogenous organic compounds applied to the soil change to nitrates with greater or less rapidity, and in this form are readily taken up by the plant.

Ammonium salts also can be assimilated by plants. German millet, golden millet, watermelons, corn, common sorrel, and other plants, seem to be able to assimilate ammonium salts directly. Ammonium salts also are converted to nitrates when placed in the soil.

While some plants can assimilate free nitrogen, others organic compounds, and still others nitrogen in the form of ammonia, nitrates appear to be the form in which nitrogen is taken up with the greatest readiness by most plants. It is also the form which all nitrogen compounds finally assume when placed in the soil.

When combined nitrogen, in whatever form of combination, is placed in the soil, it is converted into ammonium salts, nitrites, and finally nitrates, with greater or less speed, depending on the form of combination, the temperature, condition of the soil, etc., provided certain living organisms are present (and they usually are). If in any given soil, we determine the relative rate with which nitrogenous fertilizers which cannot be utilized directly by the plant, are converted into nitrates, it should throw some light upon the relative values to plants of those particular fertilizers. This is the object of the work which will be described in the following pages.

HISTORICAL.

Müntz and Girard[1] have determined the relative rate of nitrification of some fertilizers. A small quantity of the fertilizer was intimately mixed with natural soil, and kept at the temperature of 15°–25° C., properly moistened, and at the end of a given period leached with water, and the nitrate determined in the extract. The nitrate existing in the soil at the beginning of the experiment was previously determined. The time was 30, 32, and 39 days for different sets. The nitrogen converted into nitrates, and the nitrogen recovered from the soil by horse-tooth corn in two years, is shown in the following table:

[1] *Central-Blatt agr. Chem.*, **20**, 656 (1891) abs.

	Nitrified in 30 days. Per cent.	Recovered by corn. Per cent.
Ammonium sulphate	75.0	76.7
Dried blood	72.4	55.0
Roasted horn, fine	71.0	60.1
Flesh meal	70.4	....
Horn trimmings, fine	55.5	53.3
Poudrette, rather coarse	18.1	14.9
Roasted leather, fine	11.6	38.3
Leather chips, raw	0.4	....

In another series, the order of nitrification was as follows: Bat guano, dried grasshoppers, dried cockchafers, flesh meal, dried blood (the substance nitrified to the greatest extent being given first). There is very little difference between the three substances named last. The nature of the soil has a great influence on the change. Nitrification was most active in a light soil from Joinville (used in the experiment referred to above), then in a garden soil, then in a chalky soil, then in a marled moor soil. Very little nitrification occurred in a very calcareous clay, except with cow manure, and yellow lupines, which loosened their texture; and none in an acid moor soil, with the same two exceptions.

P. Bonâme[1] determined the nitrates in the drainage water from a sandy soil deficient in lime to which fertilizers had been added. The order of nitrification at the end of the first month was found to be,—fish guano (most rapid), blood, fertilizer, oil cake, and ammonium sulphate. When calcium carbonate was added, nitrification took place more rapidly, but the order was still dried blood, oil cake, ammonium sulphate (see Table I).

TABLE I.

Nitrate nitrogen in 100 grams soil (in mg.)

	One month.	Two months.	Three months.
Soil	4.2	5.0	5.0
Soil and ammonium sulphate	22	29	35
Soil and dried blood	66	74	85
Soil and oil cake	59	82	95
Soil and fish guano	74	110	113
Soil and calcium carbonate	6.2	7.3	6.0
Soil, calcium carbonate, and ammonium sulphate	75	133	186
Soil, calcium carbonate, and dried blood	123	151	159
Soil, calcium carbonate, and oil cake	97	139	137

[1] *Expt. Sta. Record*, **9**, 732 abs.

It will be noted that where calcium carbonate was not used, nitrates were formed more slowly through the entire period from ammonium sulphate than from the organic substances used. When calcium carbonate was added, the quantity of nitrates produced for the first and second months from ammonium sulphate was smaller than from the organic substances. At the end of the third month, a larger quantity of nitrates was formed from ammonium sulphate than from organic materials.

EXPERIMENTAL.

Effect of Dilution of Soil.—The effect of ratio of soil to fertilizer was studied in some preliminary experiments. 3000 grams of a sandy soil from a pasture, which had been sifted through a 6-mesh sieve, was mixed well with the quantity of dried blood containing 1.0, 0.5, 0.25, gram nitrogen, and the mixtures placed in a dark closet for fourteen days. They were watered at suitable intervals, endeavoring to maintain the original 10 per cent. of water. The temperature was about 27° C. The nitrates were leached out at the end of the period, and their quantity determined by the Tiemann–Schulze method. Results are given in Table II.

TABLE II.

	Dilution.	Nitrates. Gram.	Nitrified. Per cent.
Soil	....	0.0963	....
Soil and 1.0 gram nitrogen	$^1/_{3000}$	0.4564	36.0
Soil and 0.5 gram nitrogen	$^1/_{6000}$	0.3626	52.3
Soil, 0.5 gram nitrogen, and 1.785 gram calcium carbonate	....	0.5043	81.6
Soil and 0.25 gram nitrogen	$^1/_{12000}$	0.2354	55.6

The rapidity of the nitrification is influenced very decidedly by the dilution, and increased by calcium carbonate from 100 to 156. Thirty pounds of nitrogen per acre is a liberal application for a fertilizer. Assuming that the mean weight of a cubic foot of soil is 80 pounds, and that the soil is cultivated to the depth of 6 inches, then the dilution of the nitrogen applied as a fertilizer is $^1/_{57000}$, which is much greater than in any of the above cases. But it must be remembered that a fertilizer is never mixed intimately with the soil, and is often in lumps, so that the actual soil surface in contact with the fertilizer is probably much less than $^1/_{12000}$. This would be particularly true with materials like dried blood, which are insoluble in water. Soluble fertilizers, like ammonium

sulphate, would diffuse until they become fixed, or the soil water becomes of a uniform composition; the diffusion of salts in a soil must be a very slow process.

RATE OF NITRIFICATION.

The experiments to determine the relative rate of nitrification were carried out as follows: The fertilizing materials were those sent out by the referee of the Association of Official Agricultural Chemists for 1900, to test the methods for determining the availability of nitrogen. A sandy clay soil from a pasture was sifted through a coarse sieve (6 meshes to the inch), and a quantity of material equivalent to 0.6 gram nitrogen was intimately mixed with 1000 grams of the soil. The soil was then placed in precipitating jars, and kept in a dark closet, enough water being added to raise the percentage from 6.3 to 11.6 per cent. At suitable periods, three of the jars were weighed, and the estimated loss of water was replaced in all the jars. The temperature was 28°–30° C., and the time was three weeks. When calcium carbonate was added, the amount was exactly sufficient to combine with the nitrogen of the fertilizer if the entire amount were converted to nitric acid. At the end of the experiment, the nitrates were leached out, and the amount determined by the Tiemann–Schulze method. The amount of nitrates found in a blank experiment was deducted from the total. The results are given in table III.

On account of the surprisingly small percentage of ammonium sulphate nitrified in the first series, the experiments with cotton-seed meal and ammonium sulphate were repeated, the time being twenty-six days, the temperature 23°–26° C., and the sample moistened as before. The soil was taken from the same pasture as in the first series, but differed from it somewhat, as is shown by the fact that it contained 0.1641 gram nitrogen as nitric acid per kilogram, whereas the former contained only 0.0595 gram.

RATE OF NITRIFICATION AND AVAILABILITY OF NITROGEN.

We have selected, and give below (Table III), the results obtained by vegetation tests with oats and Hungarian grass by Jenkins and Britton[1] and those obtained by Bizzell in the laboratory of this Station with the pepsin-hydrochloric acid method,

[1] *Conn. State Station Report* 1897, 357.

and the neutral permanganate method, the materials being those used in these nitrification experiments.

TABLE III.

	Rate of nitrification				Availability.		
	Without		With $CaCO_3$.		Soluble		Vegetable
Series I.	Per cent.	Rank.	Per cent.	Rank.	$KMnO_4$.	Pepsin.	Test.
Dried blood.....	34.8	100	54.9	100	94.4	94.7	73.3
Cottonseed meal...	33.9	97	54.8	100	91.1	91.1	64.8
Dried fish.....	30.3	87	46.5	85	88.7	67.3	63.9
Tankage.....	26.2	75	34.8	63	88.3	56.4	49.4
Bat guano.....	22.4	64	35.8	65	75.1	56.4	..
Bone	18.9	54	16.6	30	64.2	92.3	16.7
Bone (six weeks)...	21.7	..	17.4	..	..	..	..
Ammonium sulphate	1.3	4	31.1	55	100	100	..
Sodium nitrate.....	..	..	..	..	100	100	100
Series II.							
Cottonseed meal...	26.7	..	..	..	..	..	..
Ammonium sulphate	3.4	..	32.6	..	.	..	..

The order of availability as determined by the neutral permanganate method, and by the vegetation experiments, is the order of nitrification, except in the case of ammonium sulphate. The pepsin-hydrochloric acid method places bone next to blood, and above cottonseed meal, where it does not belong.

The mechanical condition of the material would, of course, have great effect on the rate of nitrification. It is quite possible that the organic fertilizers contain two or more nitrogen compounds of different degrees of susceptibility to the nitrifying organisms. Bone was nitrified to the extent of 18.9 per cent. in three weeks, and only 21.7 per cent. in six weeks.

EFFECT OF CALCIUM CARBONATE.

Taking the quantity of nitrates formed without the presence of calcium carbonate as 100, the quantity formed with it present was, with dried blood, 158; cottonseed meal, 162; dried fish, 153; tankage, 133; bat guano, 160; bone (three weeks), 88; bone (six weeks), 80; ammonium sulphate, 2390; ammonium sulphate (Series II), 959. This effect may depend on the quantity of bases present in the material. The rate of nitrification of bone, which contains large quantities of calcium salts, is actually decreased by the addition of calcium carbonate while that of ammonium sulphate is increased enormously. These results show the bene-

ficial influence of lime in rendering nitrogenous fertilizers available, and explain in part why lime is so beneficial to many crops.

When ammonium sulphate is used as a fertilizer, it would be advisable to add calcium carbonate at the same time, in many cases.

NITRIFICATION OF AMMONIUM SULPHATE.

As regards ammonium sulphate, in a soil deficient in lime, it is nitrified less readily than any other of the fertilizing materials tested. In the soil to which calcium carbonate had been added, the rate of its nitrification still falls below that of cottonseed meal, blood, and dried fish, and was in one series less, the other greater, than tankage and bat guano, but the average was below. In Bonâme's experiments ammonium sulphate was nitrified during the first and second months less rapidly than any of the other fertilizing materials used (blood, oil cake, guano) whether calcium carbonate was added or not. On the contrary the experiments of Müntz and Girard (presumably in a soil containing calcium carbonate) place ammonium sulphate at the head of all the fertilizing materials tested (blood, flesh meal, poudrette, roasted leather, leather chips).

There are three possible ways to account for the slow rate of nitrification of ammonium sulphate.

1. Ammonium sulphate may hinder the action of the nitrifying organism. The soil in question contained 2.5 grams ammonium sulphate dissolved in 100 grams soil water. It is known that various salts will retard the nitrifying activity of the organisms if present in too large quantity. Deherain found that common salt began to be harmful when more than 0.1 per cent. of the weight of the soil was added, and with larger quantities nitrification almost ceased. Large additions of sodium nitrate also decrease the rate of nitrification.

This explanation will not account for the beneficial action of calcium carbonate, for if double decomposition takes place, the ammonium carbonate formed is more of a hindrance to the germs than the ammonium sulphate.

The assumption that ammonium sulphate hinders the action of the nitrifying organism would explain the low rate of nitrification of ammonium sulphate that we have obtained. It would also explain the results of Bonâme (already cited), according to which

ammonium sulphate is nitrified very slowly indeed the first and second months, and very rapidly the third. In direct contradiction to the above hypothesis, however, would stand the experiments of Müntz and Girard, who found that, in thirty days, ammonium sulphate was nitrified to a greater extent than dried blood, etc., and those of Th. Schloesing.[1] The latter found that at the end of fifty-six days ammonium chloride added to a soil at the rate of 3.58 grams per kilo (1.8 grams per 100 cc. of soil water) was almost completely nitrified, and the same occurred with ammonium sulphate at the rate of 2.7 grams per kilo (1.4 grams per 100 cc. soil water) in twenty-two days, and ammonium carbonate at the rate of 0.53 gram ammonia per kilo in twenty-eight days. The soil contained 19.4 per cent. water.

These difficulties might be explained by supposing that the ammonium sulphate affects the nitrifying germs less in some soils than in others, either on account of the different character of the soils (power of fixing ammonia, etc.) or the presence of different kinds of nitrifying organisms.

If the ammonium sulphate is detrimental to the nitrifying organisms, the same kind of action would take place when it is used as a fertilizer though perhaps to a less degree. Each lump of the salt would become a center from which would diffuse a solution of ammonium sulphate, detrimental to the nitrifying organisms. The time required for this unfavorable condition to disappear, would depend on the rate of diffusion of the salt, soil moisture, rainfall, etc.

2. The second explanation for the slow rate of nitrification of ammonium sulphate compared with the other materials, is that the nitric and sulphuric acids formed are detrimental to the nitrifying organisms, being only neutralized in part by the bases of the soil. When calcium carbonate is added, it neutralizes the acids, with consequent acceleration of the change. This explanation is probably applicable, but does not explain all the facts, for if so, the addition of calcium carbonate would remove the unfavorable conditions, and place ammonium sulphate at the head of the list, which it does not do.

3. The third explanation is, that different soils contain different nitrifying organisms, some of which convert organic matter directly to nitrites, while others change ammonium salts to

[1] *Central-Blatt agr. Chem.* **19**, 1 (1890) abs.

nitrites more readily. The nitrites are then converted to nitrates. In soils containing the first kind of organisms, and few of the second, organic matter would be converted to nitrites more rapidly than ammonium salts would be, as was the case in the experiments of Bonâme, and those here described. In soils in which the second class of organisms predominate, ammonium salts would be nitrified more rapidly than organic compounds. This hypothesis would explain all the experiments here cited.

It appears very probable that all three of the explanations given above apply, and that all three are in operation, one exerting a greater influence in some soils than others. It is the purpose of this Station to continue the experiments on nitrification, with a view to test all the problems that may arise.

CONCLUSIONS.

1. The nitrification of blood takes place more rapidly when it is mixed with a large quantity of soil, than with a small quantity.

2. The order of nitrification in the soil used was, dried blood (most nitrified), dried fish, tankage, bat guano, bone, ammonium sulphate. Excluding the ammonium sulphate, this is the order of availability, as measured by vegetation tests, and solubility in potassium permanganate.

3. When calcium carbonate was added to the soil, the nitrification was greatly accelerated, and the order became, dried blood, cottonseed meal, dried fish, bat guano, tankage, ammonium sulphate, bone.

4. When ammonium sulphate is used as a fertilizer, in most cases it would be advisable to add calcium carbonate in some form also.

5. The low rate of nitrification of ammonium sulphate is probably due to the presence of organisms which nitrify organic compounds in preference to ammonium salts. The presence of the ammonium sulphate may also hinder the activity of the nitrifying organisms. The acids formed may also be a hindrance when no base is present to neutralize them. All three of these causes may be in operation at the same time.

AN ELECTRICALLY HEATED AND ELECTRICALLY CONTROLLED THERMOSTAT.

By S. W. Young.

Received April 3, 1901.

I RECENTLY found myself, on account of a very irregular and inferior gas supply, forced to devise some other means than the one usually employed, for heating and regulating the thermostat. After a few preliminary experiments the apparatus herein described was developed, and has, after considerable experience, shown itself to be thoroughly satisfactory,—in many respects more satisfactory than the usual form with gas-heating.

For this latter reason it seemed worth while to publish a brief description of the apparatus, in the hope that use might be made of it by others. As will be readily seen, the principle allows of very ready application to thermostats for biological laboratories, such as are used for the purpose of maintaining constant temperatures in paraffin baths for imbedding, etc., and for incubators and the like. Some forms of the apparatus for these purposes are being tested and, if successful, will perhaps be described elsewhere, later.

The apparatus consists of four essential parts : (1) the bath (not shown in diagram); (2) the heater; (3) the interrupter; (4) the regulator.

1. *The Bath.*—This may be of any desired form. For my purposes, I used a cylindrical agate-ware can covered with felt. The capacity was about 30 to 35 liters. The general arrangement of the bath is identical with that of the usual Ostwald thermostat and needs no further description.

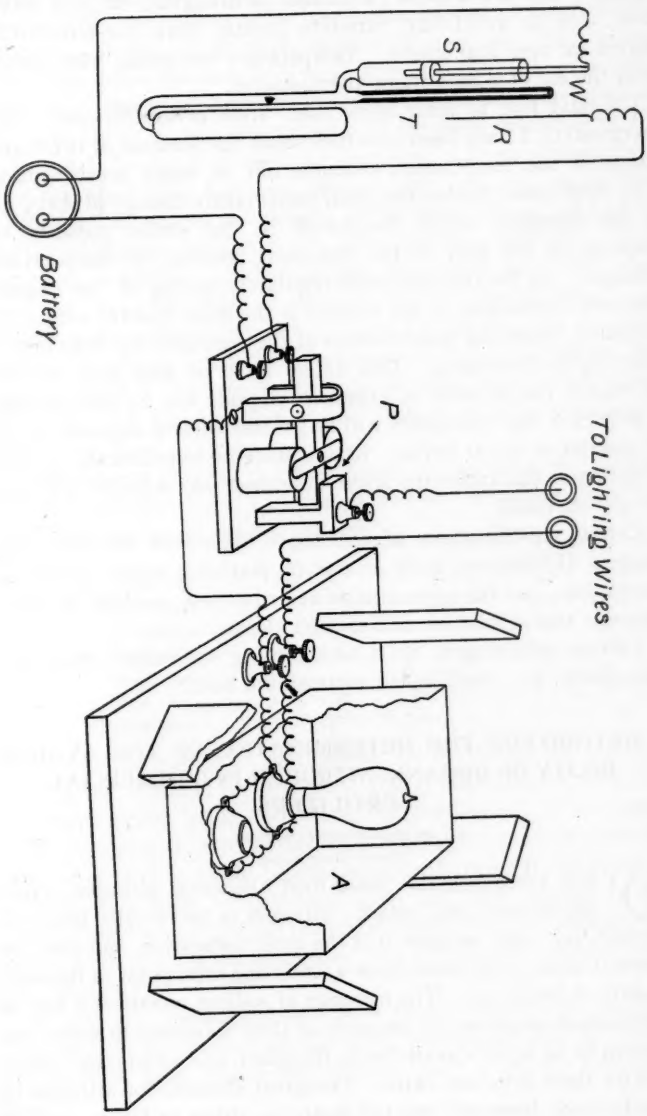
2. *The Heater.*—This consists of a square board of convenient dimensions, upon which near the center are screwed two or more incandescent light receptacles, which are wired up parallel, as usual. Surrounding these is an asbestos box open at top and bottom, which serves to economize heat. For heating purposes incandescent lamps are used and have been found very satisfactory for low temperatures, although it may be questionable whether they would prove sufficiently durable at higher temperatures. For maintaining my 30-liter thermostat at 25° C., I have found that one 16 c. p. and one 8 c. p. 100 v. lamp acting

together were wholly sufficient. The four uprights at the corners of the base-board serve as supports for the bath.

3. *The Interrupter.*—This I made by the reconstruction of a telegraphic sounder. The wiring of the current to the lamps is so arranged that when the armature is raised the current passes through it and the lamps remain lighted. When the armature is pulled down the current to the lamps is interrupted at P, and the lights go out. It goes without saying that platinum contacts are preferable.

4. *The Regulator.*—This is a modification of the ordinary form of the gas regulator. The principal modification lies in the side tube S. This is provided with a piston carrying a stout iron or platinum wire W. In filling the regulator, it is so arranged that the whole space below the piston is filled with mercury and a layer of mercury is placed on the top of the piston. This allows: (1) connection between the mercury of the regulator and the battery cell; (2) it allows of the regulation of the height of the mercury in the capillary tube T, by raising and lowering the piston. In this way the regulator can be set for any desired temperature. The piston may be made of a piece of cork, fastened to the wire by cement. There is no particular difficulty in making such a piston mercury-tight. Finally the wire R is so arranged that it can be placed at any desired height in T. It serves to complete the circuit through regulator, battery, and interrupter when, by warming, the mercury shall have risen in T to such a height that contact is made with R. It also serves for the final, exact regulation of the temperature.

The action of the whole apparatus is then as follows: The bath is placed over the heater and the regulator in the bath (which must naturally be mechanically stirred); the current is turned on through the lamps which warm the bath; this warming expands the mercury and toluene in the regulator, until finally contact is made between the wire R and the mercury in T; this closes the circuit through the battery and interrupter, drawing down the armature of the latter and interrupting the current through the lamps; cooling follows, the contact between the mercury and R is broken and the current again made through the lamps. Thus the temperature in the bath is maintained constant to within small limits. In general the temperature of my thermostat never varied more than from two- to three-hundredths of a degree. By


S
W
T
R
Battery
P
To Lighting Wires
A

taking special precautions (avoidance of draughts, etc.), I have been able to avoid any variation greater than one-hundredth degree for over four hours. Temperature variations were noted with the aid of a Beckmann thermometer.

I should like to state here that, from my experience with thermostats, I have been convinced that the fineness of the regulation of the temperature demands not so much sensitiveness, *i. e.*, large linear motion for small temperature change in that part of the regulator where the cut-off is, but rather rapidity of response on the part of the expansive medium to temperature changes. In the ordinary bulb regulator, the lag of the expansion and contraction of the toluene is the most fruitful source of variation, when the sensitiveness of the regulator has been otherwise highly developed. This defect is to be best met, not by increasing the quantity of expansive liquid, but by distributing it in such a way that there will be greater surface exposed; *i. e.*, in annular or spiral bulbs. I have made no experiments in this direction as the apparatus above described was wholly sufficient for my purposes.

Certain modifications of the above apparatus will naturally suggest themselves, such as use of platinum wires instead of lamps, etc., but the apparatus as described has worked so satisfactorily that I have let well enough alone.

Certain advantages, such as affording no danger from fire, cleanliness, etc., need not be enumerated here.

A METHOD FOR THE DETERMINATION OF THE AVAILABILITY OF ORGANIC NITROGEN IN COMMERCIAL FERTILIZERS.

BY JOHN PHILLIPS STREET.

Received March 12, 1901.

OF the three essential plant-food elements, nitrogen, phosphoric acid, and potash, nitrogen is by far the most important, not only because it is the most expensive, but also because it is the chief factor from a fertilizing standpoint in the early growth of the plant. The nitrogen of sodium nitrate and that of ammonium sulphate, on account of their solubility in water, are known to be readily available to the plant, and satisfactory methods for their detection exist. The great demand for nitrogen by the farmers, however, and the desire to utilize as far as possible

all by-products have led fertilizer manufacturers to search for forms of organic nitrogen for use in the mixing of their various brands. Among those most commonly used are dried blood, dried fish, castor pomace, hoof meal, ground bone, tankage, cottonseed meal, and linseed meal. Practical experience has shown all of these forms of organic nitrogen to be quite available to the plant, and has marked them as excellent sources of plant food. The manufacturers, however, did not stop with the use of these materials, but sought still others, which were cheaper, and whose bulk was of great assistance as a filler in their fertilizers. Such materials as garbage, leather, shoddy, felt waste, and hair, came into use, and while their employment has been by no means general, it is nevertheless important to agricultural chemists that they should be able to detect these materials in mixed fertilizers, for vegetation tests have shown them to be either entirely worthless, or at any rate not available to the plant until after a comparatively long lapse of time.

The analyses made at the New Jersey Experiment Station during 1900, showed that the cost per pound of the nitrogen in different organic materials was as follows:

	Cents.
Dried blood	14.2
Dried fish	13.7
Cottonseed meal	14.5
Ground bone	16.4
Wool waste	7.0 to 0.5
Hair	5.1 to 4.6
Leather	5.0

The present laboratory methods do not determine the source of the organic nitrogen in fertilizers, and it is evident at once that the manufacturer using wool waste, hair, or leather, as the source of his nitrogen, is not justified in charging for that nitrogen the same price that he would be warranted in charging if the nitrogen of blood, fish, bone, or cottonseed meal had been utilized in making his fertilizers. To call this simply total nitrogen is manifestly unfair to the honest manufacturer, and at the same time misleads the purchaser.

At both the Connecticut and New Jersey Experiment Stations the complete fertilizers analyzed during one season were subjected to digestion with pepsin-hydrochloric acid, with the following results:

Connecticut. Per cent. soluble.				New Jersey. Per cent. soluble.			
3	over	90		3	between	80 and	90
22	between	80 and	90	13	"	70 "	80
62	"	70 "	80	16	"	60 "	70
18	"	60 "	70	11	"	50 "	60
12	"	50 "	60	4	"	40 "	50
6	"	40 "	50	2	under	40	
2	under	40					

A fertilizer showing 60 per cent. of its organic nitrogen soluble in pepsin may be considered as above suspicion, and one falling as low as 50 per cent. must not necessarily be condemned, while one below 50 per cent. must be regarded as suspicious. From the above table it will be seen that in Connecticut eight samples, or 6 per cent., fall in the suspicious class, and in New Jersey 6, or 12 per cent. These results show that, although their number is limited, there are suspicious fertilizers on the market, and that the necessity does exist for an accurate method to determine nitrogen availability.

For many years, therefore, agricultural chemists have employed the above-mentioned pepsin-hydrochloric acid method,[1] generally used in biochemical laboratories, as a test of the availability of organic nitrogen. Vegetation tests, and chemical tests by this method on the same materials have in general shown close agreement in most classes of organic nitrogenous compounds, but experiments at the Connecticut and New Jersey State Experiment Stations have shown that for certain classes of materials, notably hoof meal, it gives but little indication of their value. The following tabulation shows some comparative results obtained by the writer on certain well-known materials:

	Availability by Vegetation tests.	Pepsin. digestion.
Dried blood	68	68
Dried fish	66	51
Hoof meal	62	39
Steamed bone	60	56
Tankage	59	56
Wool waste	31	22
Raw leather	2	14

A comparison of these results shows that with the exception of raw leather, the pepsin method tends to give lower results than were secured by the vegetation tests. The pepsin results, how-

[1] Report of Conn. Expt. Station, 1893, 219.

ever, are quite satisfactory, except in the case of hoof meal, where the pepsin solubility is 23 per cent. lower than by the actual culture test.

Not only is the pepsin-hydrochloric acid method unreliable with certain materials, but it is so chronokleptic that its use is almost impossible in the average agricultural or commercial laboratory. The putrefactive method, employed in several laboratories, is open to these same objections.

While the writer was referee on nitrogen for the Association of Official Agricultural Chemists in 1895, Mr. S. H. T. Hayes, of Cornell University, submitted to him a paper in which he tested various methods for determining availability, including fractional treatment with sulphuric acid, digestion in a saturated solution of barium hydroxide, and digestion in alkaline, acid, and neutral solutions of potassium permanganate. The results obtained by Hayes[1] were not at all conclusive, but those secured by the permanganate digestion were promising, and were deemed by the writer worthy of further trial.

DIGESTION WITH POTASSIUM PERMANGANATE.

The method, as outlined by Hayes, consists in treating 1 gram of the material in a 500 cc. flask with 100 cc. of potassium permanganate solution, containing 16 grams potassium permanganate and 200 grams caustic soda per liter. Digest at a low temperature for one hour, then increase the temperature and distil for one hour, and titrate as usual. For the acid solution, the method consists in weighing 1 gram of material into a 500 cc. flask, add a little paraffin and 100 cc. of potassium permanganate solution (16 grams potassium permanganate and 100 cc. concentrated sulphuric acid to the liter). Connect with distilling apparatus, and heat at a temperature just below boiling for one hour. Then add 50 cc. of saturated caustic soda solution, distil for thirty minutes, and titrate as usual.

After making a number of tests, it was evident that the methods, as suggested, were difficult to control. It was almost impossible to carry on the digestion without a boiling of the liquid, and it was very difficult to maintain uniform conditions in two different sets of tests. Comparative results obtained by seven agricultural chemists working in different laboratories showed a wide divergence, and it was believed by the writer that this was

[1] U. S. Dept. of Agr. Dept. of Chem. Bull., 47, 112-116.

due more to this inability to control the temperature, and keep the conditions uniform, than to any inherent defect in the principle of the method itself.

It also seemed that the great variations in bulk of the nitrogenous materials examined required that the comparison should be based on the same quantity of organic nitrogen rather than on equal weights of materials. With these ideas in mind, the writer devised the following method :

Weigh an amount of the material equivalent to 0.075 gram of nitrogen into a 500 cc. Erlenmeyer flask, add 100 cc. of neutral, 1.6 per cent. potassium permanganate solution, and digest on a steam-bath for thirty minutes, shaking occasionally to moisten any particles of the material adhering to the sides of the flask. Filter and wash thoroughly, using from 125 to 150 cc. of water. Determine the total nitrogen in the undigested residue by the ordinary Kjeldahl method.

Mr. C. H. Jones,[1] of the Vermont Experiment Station, has also modified Hayes' method, by using an amount of the material equivalent to 0.045 gram of organic nitrogen with the alkaline potassium permanganate solution. The results secured by this method have on the whole been very acceptable, but with cotton-seed meal, a material of known value, it fails utterly as a test of availability.

To test the method suggested by myself, I have examined eighty-four samples of organic nitrogenous matter, representing twenty-eight different classes of fertilizing material. The results will be found in the table below, where the total organic nitrogen and the percentage digestibility in potassium permanganate are given.

AVAILABILITY OF ORGANIC NITROGEN.

	Organic nitrogen. Per cent.	Digestible. Per cent.
Dried blood	12.41	95.6
" "	13.20	95.2
" "	14.01	95.0
" "	13.60	94.4
" "	13.73	94.3
" "	14.04	94.0
" "	11.63	91.9
" "	11.39	91.8
" "	13.10	91.0

[1] U. S. Dept. of Agr., Div. of Chem., Bull. 57, 51.

	Organic nitrogen. Per cent.	Digestible. Per cent.
Dried blood	13.41	89.8
" "	11.06	87.4
Average	12.87	92.8
Ground horn	14.85	95.9
Concentrated tankage	11.13	93.7
Ammonite	13.00	93.6
Cracklings	13.22	93.5
Hoof meal	14.47	92.2
" "	14.04	89.7
Average	14.26	91.0
Castor pomace	6.12	90.0
Peanut pulp	8.52	89.3
Dried fish	8.78	90.2
" "	7.97	90.0
" "	7.53	88.7
" "	8.80	88.5
" "	9.53	88.0
" "	8.69	87.6
" "	7.39	87.1
" "	6.82	86.7
" "	8.28	86.5
" "	8.83	86.3
" "	9.43	86.1
" "	4.57	86.0
" "	8.37	85.0
" "	7.80	84.7
" "	6.50	82.9
" "	8.34	82.3
" "	7.75	82.2
" "	8.23	82.1
" "	5.07	81.9
" "	8.44	81.4
" "	7.49	79.6
" "	6.82	78.4
" "	5.07	74.7
" "	6.47	74.4
" "	6.86	70.1
" "	5.19	69.3
" "	6.96	65.8
Average	7.48	83.9
Tankage	6.90	91.5
"	7.67	89.5
"	5.88	87.1
"	6.42	85.4

	Organic nitrogen. Per cent.	Digestible. Per cent.
Tankage	5.69	84.0
"	6.65	81.8
"	5.67	79.8
"	5.89	79.7
"	5.34	79.7
"	5.16	65.0
Average	6.13	82.4
Cottonseed meal	7.33	79.6
" "	6.74	78.6
Average	7.04	79.1
Linseed meal	5.94	77.7
Horse meat	4.29	70.4
Steamed bone	2.78	87.0
" "	2.25	84.8
Button bone	3.33	84.0
" "	3.93	76.0
Raw bone	3.40	66.9
" "	4.12	66.3
" "	4.05	66.2
Bone sawings	3.85	77.6
Soft bone	2.37	71.6
Dissolved bone	1.95	62.7
Wool waste	2.58	77.6
" "	2.52	75.1
" "	2.51	75.0
Dissolved tankage	5.02	65.9
" "	2.93	63.1
King crab	8.78	72.5
" "	9.12	52.5
Hair manure	5.76	54.6
Garbage fertilizer	2.95	59.2
" "	3.20	44.1
Burned garbage	1.95	51.5
Steamed leather	6.87	39.5
Treated leather	7.22	33.4
Raw leather	7.56	25.5

These results are remarkably striking, the difference in the effect of the permanganate solution in the various ammoniates being very noticeable. The percentage digestibility varies from 95.9 per cent. in horn to 25.5 per cent. in raw leather. The other materials range in availability between these limits in the approximate order vegetation cultures would lead one to expect. The ground horn sample is, perhaps, somewhat above the average of

that material, it having been carefully prepared in my laboratory, and being nearly five years old and in a pulverulent condition. Of the six classes of bone examined, steamed bone shows the highest digestibility. This is doubtless due to the fact that the process of steaming had in a large measure removed the fatty matter; raw bone, in which much fat was present, is nearly 20 per cent. lower. The availability of the dissolved bone is slightly below that of raw bone, seeming to indicate that the treatment with sulphuric acid had little favorable effect on the nitrogenous matter in the bone; the same conditions obtain in the case of dissolved tankage, which shows a digestibility 18 per cent. lower than the untreated tankage. The remaining materials occupy about the rank agricultural experience would assign them.

It must be remembered in using this method, that the figures obtained are relative, not absolute. It is not claimed that it shows the exact amount of organic nitrogen available to the plant, but it does serve as a means of distinguishing high-class from low-class ammoniates. The results would seem to indicate that in any material showing by this method a digestibility of 60 per cent., or under, the nitrogen was obtained from an inferior source. It certainly could not have been obtained from blood, hoof meal, dried fish, tankage, or cottonseed meal, but was probably furnished by hair, garbage, leather, or some very inferior bone.

The table also shows the variations which may be found in working with materials of the same class, and indicates that the name of a fertilizer is not always a safe guide for the agriculturalist. The variations are particularly striking in the case of fish and tankage, where the digestibility ranges from 90.2 to 69.3 and 91.5 to 65.0 per cent., respectively. These variations are doubtless due to the varying amounts of fatty material in these products, and show still further the value of this method in the detection of such conditions.

Experiments have shown that this method is equally applicable to complete fertilizers, the only variation being that the material is washed on a filter with cold water, prior to the digestion, to remove such soluble salts as might interfere with the subsequent action of the permanganate.

It is admitted that the only true test of the availability of any fertilizer is the plant itself, but it is manifest that this method of examination is not open to all analysts, and to most is an impossi-

bility. It is hoped, therefore, that this simple method may be of value in furnishing chemists with a means of determining within reasonable limits the relative availability of the various nitrogenous materials submitted to them for examination.

LABORATORY OF THE NEW JERSEY STATE
EXPERIMENT STATION,
March 5, 1901.

AN APPARATUS FOR DETERMINING FAT.

BY H. J. WHEELER AND B. L. HARTWELL.

Received February 10, 1901.

THE Knorr apparatus[1] for the extraction of fat, which was a great improvement over preceding forms, enabled one to dispense with the ground-glass and cork connections formerly in use, by the employment of a mercury seal.

The mercury is carried in a channel which encircles the neck of the flask at the base. In order to maintain the connection between the flask and the glass part immediately above it, the two are held together by rubber bands. To avoid the use of the bands the condensers may be made movable so they can be lowered sufficiently to connect with the flasks, or if the condensers are stationary the bath which supports the flasks may be made movable. In many instances, particularly in the case of batteries of considerable size, neither of these plans is convenient and at the best, unless great care is exercised, the flasks are liable to break during the adjustment. The use of rubber bands is unsatisfactory owing to their liability to slip or break.

A later modification of the Knorr flask was one which had a glass channel attached to the neck of the flask near the top. This modification enabled one to reduce the quantity of ether liable to collect outside of the neck, but the flask was necessarily fragile and expensive. The apparatus described below was designed to remove some of the difficulties connected with that devised by Knorr and to accomplish certain other desirable objects. The improvements attempted may be summarized as follows:

1. The use of a simple flask which can be readily cleaned and replaced at small expense.

2. The employment of a rubber cup to carry the requisite

[1] Bull. 28, U. S. Dept. of Agriculture, Div. of Chemistry (1890), p. 96.

amount of mercury for sealing, and at the same time bind the flask firmly to the other parts of the apparatus.

3. The reduction to a minimum of the amount of ether, which can collect around the outside of the neck of the flask, by the ready adjustment of the cup to any point upon the neck.

4. The bending of the end of the tube from which the liquid ether drops upon the substance which is undergoing extraction, so that the ether will be delivered from the center and not flow down the glass.

5. The prolongation of the tube mentioned in (4) so that it may support the upper ends of extraction tubes or thimbles of different lengths.

6. The collection of the ether in one receptacle at the end of the extraction without disconnecting the apparatus.

7. The maintenance of the ether in a dry condition.

8. The loss of the least possible amount of ether vapor during the extraction and at its close.

Below is given a description of an apparatus designed to meet the conditions just mentioned. This apparatus, made in accordance with our specifications by Richards & Co., of New York, has already been in successful operation at considerable intervals for more than a year without apparent depreciation in the quality of the rubber cups and without the breakage of an extractor or other expensive glass parts.

A. A plain flask of 50 to 60 cc. capacity, having a straight neck.

B. A rubber cup channeled to carry mercury for sealing the connection between the flask and the lower portion F of the extractor.

C. A channel for mercury, showing the latter forced upward by the glass so as to cover the rubber, at the same time sealing the connection between the neck of the flask and the glass extractor which passes into the rubber cup at the outer margin of the channel.

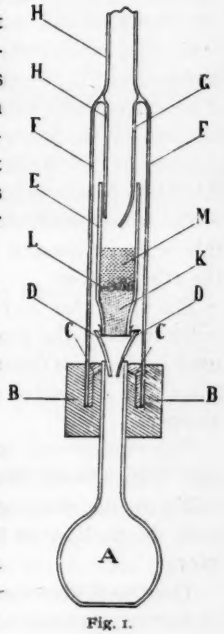


Fig. 1.

D. A small funnel to conduct the ether and dissolved fat into the flask. This is grooved where it enters the neck of the flask so that the small amount of ether which accumulates between the neck and the extractor may flow downward.

Resting upon the funnel D is the thimble which contains the material K to be extracted. The bottom of this thimble is covered with fat-free filter-paper fastened to the outside of the thimble by means of wire. The ends of the wire rest upon the edge of the funnel so as to leave space for the passage upward of ether vapor.

L. Fat-free cotton to facilitate the distribution of the ether at the beginning of or during the extraction.

M. Ether, which is maintained above the substance K in considerable quantity during most of the period of extraction. This is accomplished by raising the temperature of the flask A so that the ether may evaporate as rapidly as it filters into the flask.

E. The glass extraction tube or thimble.

F. Walls of the lower portion of the extractor.

H. The lower end of the condensing portion of the extractor, perforated at G to permit ether vapor to pass upward, and bent at an angle at the bottom so that the drops of liquid ether are delivered at the center. This part serves as a support for the thimble and is made sufficiently long to permit of the use of thimbles of various lengths.

The upper condensing portion of the extractor is of straight thin-walled glass and sufficiently long to insure condensation of the ether vapor.

The apparatus may be used singly or in battery form. The outer tubes of the condensers may be of glass, but if hot water is used in them, as described later, they should be made of metal. They are connected with the inner ones by means of rubber stoppers.

The rubber cup B binds the flask firmly to the extractor, so that rubber bands or devices for lowering or raising the bath below or the condensers above for maintaining the connection with the flask, as in the Knorr apparatus, are rendered unnecessary.

The cup also carries continually in its channel a proper amount of mercury for sealing.

In connecting and disconnecting the flask a straight cork fitting the inside of the neck of the flask A is inserted to prevent anything from falling into it as it passes through the rubber cup.

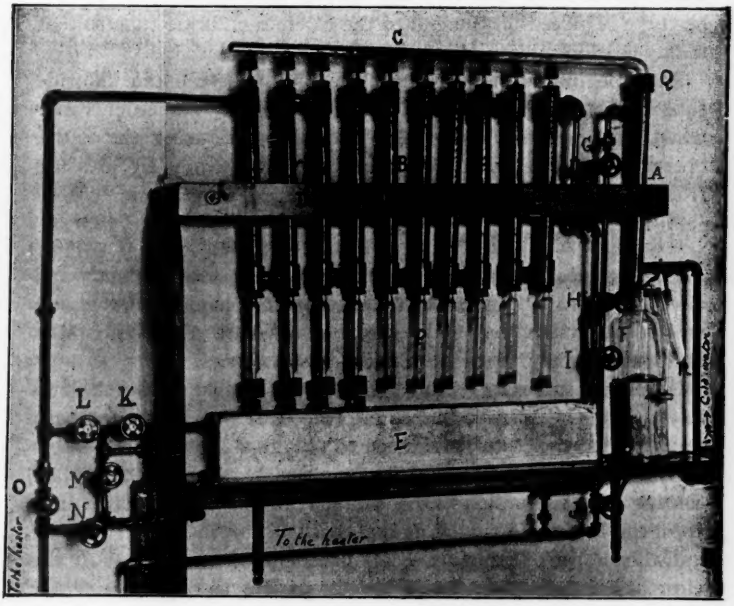


Fig. 2.

Fig. 2 shows a battery of extractors so arranged that the ether may, without disconnecting the flasks, be distilled at the close of the extraction and collected practically free from moisture. The source of heat for all the operations is an instantaneous water heater located somewhat below and (to avoid danger from fire) to the left of the battery.

BATTERY WITHOUT ARRANGEMENT FOR RECOVERING ETHER.

In laboratories where many fat determinations are made, the use of extractors in battery form is desirable. If, owing to the nature of the material to be extracted, the amount of ether necessary is considered too small to render its recovery unprofitable all of the piping necessary is that required to conduct water to

and from condenser B, and to connect the instantaneous water heater with each end of the bath E. If the apparatus is used in this manner the condenser A may be omitted, and the calcium chloride tube R attached directly to the right-hand end of tube C, which in that case may be made shorter than otherwise. A rubber tube is placed on the end of the calcium chloride tube so that it may be closed by means of a pinch-cock.

After beginning the extraction the end of the calcium chloride tube is kept open until the extractors are filled with ether vapor when it is closed and need not be opened again during the entire operation. If preferred, an automatic valve opening by pressure from within may replace the rubber tube and pinch-cock.

BATTERY COMPLETE AS SHOWN IN FIG. 2.

For the recovery of the ether the condenser A is necessary and also additional piping. The detailed arrangement of the piping will be determined by the location of the heater, the waste pipes and water supply pipes in individual laboratories.

As shown in Fig. 2, cold water after passing condenser A flows to the water heater and thence into the bath E. When the bath is once filled the water is allowed to pass through the condensers B to the waste pipe located below and to the right of valve K. During the extraction a continuous circulation is maintained from the lower right-hand end of bath E to the water heater, and thence back through the left-hand end of the bath. At the close of the extraction the cold water passing through condenser A flows to the water heater, thence to the left-hand member of battery B, forcing the cold water out underneath bath E into the waste pipe. As soon as hot water appears in the last member of battery B at the right, the current is diverted into bath E to vaporize the ether and assist in driving it over through condenser A. The water-level in bath E in the meantime is controlled by valve K in the pipe leading from the bottom of the bath to the waste; this pipe may also serve to siphon the water from the bath.

The inner tube of condenser A is straight and small enough to pass inside of tube C at the point Q where the latter is turned downward to meet it. This connection is sealed by mercury just as in the case of the flask and extractor (Fig. 1).

The tips of the inner tubes projecting through the tops of the

metal condensers B are drawn down so that they can enter the downward projections on the tube C. Short pieces of heavy-walled rubber tubing are slipped over these, and over the pieces of tubing are passed bored rubber stoppers which clasp them and the outside of the downward projections of tube C. The stopper projects considerably above the tubing so as to form a cup (about the tip) which holds sufficient mercury to produce a perfect seal over the rubber and between the two glass parts.

In setting up the apparatus the extractors P may be inserted in the condensers B before the latter are clamped in position.

The flask F is connected with the inner tube of condenser A by an ordinary cork coated with plaster of Paris. The only vent to the apparatus during the extraction and distillation is through the calcium chloride tube R attached to flask F which is kept closed the entire time after the apparatus has first been charged with ether vapor. By this arrangement no odor of ether can be detected except when the flasks are being changed and for a few moments after the extraction begins. After removing a flask from the extractor another should either be attached immediately or else the lower end of the extractor closed by means of a stopper to prevent unnecessary escape of ether vapor. It is desirable to insert a second flask at once in order that oxidation of the mercury by exposure to the air may be avoided as far as possible. In case the bath E is full of water, the extraction tube may be introduced or removed from the extractor without wetting by sliding it partially into a test-tube.

RHODE ISLAND COLLEGE OF AGRICULTURE AND MECHANIC ARTS.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF LAFAYETTE COLLEGE.]

METHOD FOR PREPARING STRICTLY TENTH-NORMAL, FIFTH-NORMAL, ETC., HYDROCHLORIC OR NITRIC ACID.

BY RICHARD K. MEADE.

Received April 10, 1901.

IN a paper before the Lehigh Valley Section of the Society,[1] the writer described a method for preparing strictly normal, semi-normal, decinormal, etc., sulphuric acid by decomposing copper sulphate with the electric current. Since the publication of this

[1] This Journal, **23**, 12.

paper, the following method, depending primarily upon the same reaction, has been tried and found successful, for preparing one-fifth and one-tenth normal hydrochloric and nitric acid.

The method of procedure in making tenth-normal hydrochloric acid is as follows:

12.487 grams of pure crystallized copper sulphate are dissolved in 500 cc. of distilled water in a lipped beaker capable of holding about a liter. Into this solution, after cooling if necessary, is introduced a cylinder of copper foil attached to the negative wire of an electric circuit, and a platinum rod attached to the positive wire. Both the cylinder and rod should reach to the bottom of the beaker. The copper cylinder is made from copper foil. The writer used foil 0.015 inch thick and 3 inches wide. The foil is cut the required length, which will be about three times the diameter of the beaker plus ½ inch for a lap. The foil is curled so that the ends lap. Holes are punched through the two thicknesses of foil with a sharp nail and wire run through these so as to fasten the two ends together. The beaker is covered with a watch-glass perforated to allow the rod to enter, and a current of from one to one and a half amperes passed through the solution for from six to eight hours or all night if the decomposition is begun in the afternoon. At the expiration of this time, the watch-glass is removed and rinsed off together with the cylinder and rod into the beaker. The solution is then transferred to a liter-graduated flask and any copper that may have dropped off the cylinder into the beaker is well washed by decantation, rinsing the beaker at the same time into the flask. Now weigh, accurately, exactly 12.215 grams of crystallized barium chloride into a small beaker, dissolve in water and pour into the flask. Dilute the latter to the mark, add 2.6 cc. of water and mix well. Allow the precipitate to settle, siphon off the clear liquid through a dry tube, upon a dry filter and funnel, and catch the filtrate in a dry beaker or stock-bottle.

The method depends upon the decomposition of the copper sulphate solution by the electric current into copper and sulphuric acid. Upon adding barium chloride to this latter, double decomposition takes place, and barium sulphate and hydrochloric acid are formed. The addition of the 2.6 cc. of water after the solution has been made up to the mark, is to correct for the volume of water displaced by the precipitate.

In preparing tenth-normal nitric acid by this method, the only change that is made is in the substitution of 13.076 grams of barium nitrate for the barium chloride. The quantity of copper sulphate, of course, remains the same.

In preparing large quantities of the acid it would probably be simpler to pour the solution into a stock-bottle, provided with a siphon, immediately after adding the barium chloride or nitrate, making up to the proper volume and mixing. The solution can then be drawn off for use as wanted, after the precipitate has settled. The siphon tube must not reach so near the bottom of the bottle as to stir up the precipitate. Graduated flasks as large as two liters are carried in stock by dealers in such ware. When it is desirable to make up larger quantities of acid, ungraduated flasks can be purchased, holding as much as 10 or 12 liters. Their exact volume to any point on the neck can be found either by weighing water into them if a sufficiently large delicate balance is at hand or even by measuring water into them; the proper amounts of copper sulphate and barium chloride or nitrate can then be calculated and used to make this volume. In calibrating the flask by measuring water into it, it must be borne in mind that the ordinary flask is graduated to hold, not to deliver, the given volume. To find the volume a given flask will deliver, weigh into it say 100 grams of water from a weighing-bottle, revolve the flask so as to wet the sides, then pour the water back and drain the flask into the weighing-bottle for one minute. The loss in weight, on again weighing the water, may be taken as the correction to be subtracted from the volume which the flask is graduated to contain for the volume it will deliver. This method will be sufficiently accurate for the present purpose.

I have prepared only tenth-normal and fifth-normal acids by this method. Probably normal acid could also be prepared though the waste, due to the solution retained in the precipitate, would, of course, be greater owing to the larger volume of the latter.

In the first attempts to prepare tenth-normal acid by this method the barium chloride was added to the solution after the cylinder and rod had been removed and before making up to the liter. The solution was then filtered into the graduated flask after the precipitate had settled, and the latter brought upon the

paper and washed with hot water until the mark on the neck of the flask was reached. The solution was then cooled and made up to the liter. The solution, on testing, however, proved to be a little below the desired strength, due no doubt to the "holding back" of some of the acid by the precipitate. The method first given was then tried and gave a solution of the exact strength desired with much less labor and in much less time.

Both the nitric and hydrochloric acid solutions were tested as follows:

Fifty cc. of the acid were made alkaline with ammonia, heated to boiling, and ammonium oxalate added. No precipitate formed in any case.

Fifty cc. were heated to boiling and barium chloride added. Only a very slight cloud formed. The precipitate was allowed to stand over night in a warm place, filtered, washed, ignited, and weighed. The results on the five solutions were as follows:

No.	Solution.	$BaSO_4$ in 50 cc. Gram.	H_2SO_4 in 50 cc. Gram.	H_2SO_4 in 1 liter. Gram.
1	0.1 N HCl	0.0004	0.00017	0.0034
2	0.1 N HCl	0.0008	0.00034	0.0068
3	0.2 N HCl	0.0030	0.00126	0.0252
4	0.1 N HNO_3	0.0025	0.00105	0.0210
5	0.2 N HNO_3	0.0038	0.00160	0.0320

Where the standard hydrochloric acid is intended for use in determining the alkaline earths, it would, of course, be necessary to add a little in excess of 12.215 grams of barium chloride, the theoretical quantity necessary to convert the sulphuric acid to tenth-normal hydrochloric acid. Indeed it would, perhaps, be better in all cases to add a slight excess of the salt since a trace of it in the solution can certainly, in most cases, do no harm.

When checked against nearly tenth-normal sodium hydroxide solution (which had been prepared from metallic sodium, carefully standardized, and kept free from carbon dioxide), using phenolphthalein as an indicator, the results showed each solution prepared to be of exact strength, as the following will show:

No.	Solution.	Standard acid taken for the test. cc.	Standard sodium hydroxide required. cc.	Equivalent volume of 0.10 N NaOH.[1] cc.
1	0.1 N HCl	10.0	10.2	10.01
		10.0	10.2	10.01
		10.0	10.2	10.01
		20.0	20.4	20.02

[1] Factor for converting standard sodium hydroxide to 0.1 N NaOH = 0.9813.

No.	Solution.	Standard acid taken for the test. cc.	Standard sodium hydroxide required. cc.	Equivalent volume of 0.10 N NaOH. cc.
2	0.1 N HCl.....	10.0	10.2	10.01
		10.0	10.2	10.01
		20.0	20.4	20.02
3	0.2 N HCl.....	10.0	20.4	20.02
		10.0	20.35	19.97
		20.0	40.75	40.00
4	0.1 N HNO_3	10.0	10.2	10.01
		10.0	10.2	10.01
		20.0	20.4	20.02
5	0.2 N HNO_3	10.0	20.4	20.02
		10.0	20.4	20.02
		20.0	40.7	39.94
		20.0	40.75	40.00

EASTON, PA., April 1, 1901.

[CONTRIBUTION FROM THE CHEMICAL DIVISION, U. S. DEPARTMENT OF AGRICULTURE, NO. 40.—SENT BY H. W. WILEY.]

THE COMPOSITION OF JELLIES AND JAMS.

BY L. M. TOLMAN, L. S. MUNSON, AND W. D. BIGELOW.

Received May 3, 1901.

AS preliminary to the examination of a large number of samples of commercial fruit preserves, it was thought desirable to have, as a basis of comparison, the analyses of fruits and fruit products of known origin, as the work with this class of foods has been largely confined to the detection of adulterations rather than to the proximate analysis. Accordingly, such whole fruits as were to be obtained were purchased, and from these the juices, jellies, and jams were prepared. The juices were prepared by cooking the cleaned fruit, with enough water to prevent scorching, till it became soft, and straining through a jelly-bag. In the preparation of the jellies, equal parts of the strained juice and cane-sugar were used and were heated to the point of boiling, which required about twenty minutes.

With the jams approximately one part of sugar was used to two parts of the crushed fruit, heated to boiling, and this temperature maintained for about twenty minutes. In all cases the original fruit and sugar, as well as the final products, were weighed which gave a basis for estimating the amount of added cane-sugar in the finished product.

It is to be regretted that the fruits selected were not in all cases of typical composition. This is especially true of the apples and grapes. This, however, will not lessen their value for studying the sugar content. In comparing the composition of jellies

and jams with that of the juices and pulps from which they were prepared, allowance must be made for the changes in composition resulting from the evaporation of water and the loss of proteid and other matter in the scum that rises in the process of preparation.

METHODS OF ANALYSIS.

With the juices and thoroughly pulped fruits and jams, weighed amounts were taken for each determination. With the jellies, it was found more convenient to dissolve 50 grams of the material in water and make it up in volume to 500 cc. Then aliquot portions were taken for solids, ash, acids, nitrogen, and reducing sugars.

Total solids were determined in about 10 grams of the juice and the crushed fruits, and about 5 grams of the jellies and jams, by drying in large flat-bottomed platinum dishes at a temperature of 100° for ten to twelve hours. The writers recognize that drying in vacuo at a low temperature is preferable, but since that would be impracticable with the large volume of work planned with commercial products, it was not done with these samples. Water in sufficient quantity to make them flow readily was mixed with the portion of the jams and crushed fruit taken for the determination of total solids, so that they could be distributed in an even layer over the bottom of the dish.

To estimate the ash the residue obtained in the determination of total solids was thoroughly charred, exhausted with water, the insoluble portion washed with water and collected on a filter. The filter-paper and contents were then returned to the dish and ignited to whiteness, the soluble ash, and a few drops of ammonium carbonate solution added, and the whole evaporated to dryness, heated to low redness, and weighed.

In the estimation of acidity about 10 grams were dissolved in hot water and diluted to about 400 cc. with recently boiled water. A few drops of phenolphthalein solution were then added and the mixture titrated with a decinormal solution of potassium hydroxide. The end point was easily observed even in highly colored fruits. Owing to the dissimilarity of the various fruits in their characteristic acids, it is found advantageous to express acidity in terms of one acid instead of the acid characteristic of the particular fruit which is supposed to be present. The use of an acid, which occurs in some fruits and not in others, is likely to lead to confusion. The writers prefer the custom which

is practiced in many laboratories of expressing results in terms of sulphuric acid (H_2SO_4).

Nitrogen was determined by the Gunning method in such an amount of material as would give about 2 grams of dry matter and the result multiplied by 6.25 for the proteid content.

Reducing sugars were determined by the regular Allihn method.[1]

Cane-sugar was calculated from the direct and invert polarizations by the Clerget formula

$$S = \frac{A - B}{144 - \frac{2}{t}}.$$

Polarizations were made upon normal weights of the juices and fruits and upon half-normal weights of the jellies and jams, with the Schmidt and Haensch instrument, using a 200 mm. tube. All results were calculated to normal weights.

As is well known the sugars of the fruits are largely reducing sugars, but in all the fruits examined, except the blackberry, cane-sugar was found in varying amounts. In the orange, peach, and pineapple it was in excess of the reducing sugar.

The polarization of the Damson plum is peculiar in that the invert reading at 86° is positive, indicating an excess of dextrose over levulose, while all the other fruits have either a zero or a negative reading at this temperature.

The inversion in the preparation of jams and jellies of the added cane-sugar is of particular interest. As might be expected the extent of inversion varies in general with the amount of free organic acid present, and with the length of the time the product is heated. Still the different fruit acids vary widely in their inverting action upon cane-sugar and consequently there are some marked exceptions to the general rule mentioned above. For example, in crab apple jelly, with 0.17 per cent. acid, 58.8 per cent. of the cane-sugar was inverted, while with the orange jelly of the same acid content only 4.9 per cent. was inverted. With the fox grape jam containing 0.69 per cent. acid, 92.9 per cent. of cane-sugar was inverted, while with wild fox plum containing 1.35 per cent. acid only 53.4 was inverted. The crab apple excepted, the jams and marmalades showed a higher per cent. of inversion than the corresponding jellies, owing to the fact that they were heated for a much longer time.

[1] Bulletin 46: Rev. U. S. Department of Agriculture, Division of Chemistry.

TABLE I.—JUICE.[1]

Laboratory No.	Description of sample.	Total solids. Per cent.	Ash. Per cent.	Total acids calculated as H_2SO_4. Per cent.	Proteids (N × 6.25). Per cent.	Sugars. Reducing sugar. Per cent.	Sugars. Cane-sugar added. Per cent.	Sugars. Cane-sugar found. Per cent.	Sugars. Added cane-sugar inverted. Per cent.	Polarization. Direct at 18° C.	Polarization. Invert at 18° C.	Polarization. Invert at 80° C.
20400	Apple (fall pippin)	7.95	0.47	0.627	0.543	4.00	....	1.18	....	— 3.0	— 4.6	— 2.9
20396	Blackberry	8.54	0.52	0.978	0.350	4.34	....	0.00	....	— 1.5	— 1.6	— 1.0
20403	Crab apple	5.62	0.20	0.372	0.075	2.56	....	1.03	....	— 1.0	— 2.4	— 1.1
20428	Grape (fox)	6.67	0.49	1.686	....	2.79	....	0.37	....	— 0.8	— 1.3	— 1.1
20401	Grape (Ives seedling)	8.83	0.57	0.902	0.237	5.10	....	0.89	....	— 1.2	— 2.4	— 0.6
20397	Huckleberry	16.33	0.40	0.454	....	11.21	....	0.89	....	— 3.2	— 4.4	— 0.9
20430	Orange (Florida navel)	6.08	0.36	0.297	0.581	1.52	....	2.29	....	+ 1.8	— 1.3	0.0
20427	Peach	8.90	0.45	....	0.218	....	....	4.59	....	+ 4.0	— 2.2	— 0.7
20431	Pear (Bartlett)	11.65	0.45	0.345	0.087	5.87	....	1.18	....	— 4.8	— 6.4	— 4.0
20429	Pineapple	13.27	0.45	0.588	0.368	2.74	....	8.96	....	+ 8.4	— 3.7	— 1.1
20426	Pineapple husk juice	8.43	0.77	....	0.350	....	....	4.73	....	+ 4.1	— 2.3	— 0.7
20399	Plum (Damson)	12.72	0.63	....	0.431	4.86	....	0.51	....	+ 2.0	+ 1.3	+ 2.4
20402	Plum (wild fox)	11.23	0.64	1.576	0.137	2.87	....	2.81	....	+ 1.4	— 2.4	— 1.8
20398	Mixed fruit	6.53	0.32	0.612	0.150	2.68	....	0.59	....	— 1.0	— 1.8	— 0.9

[1] The "juice" was prepared by cooking the fruit till soft, after the addition of sufficient water to prevent scorching, and straining through a jelly bag.

TABLE II.—JELLY.

Laboratory No.	Description of sample.	Total solids. Per cent.	Ash. Per cent.	Total acids calculated as H_2SO_4. Per cent.	Proteids (N × 6.25). Per cent.	Sugars. Reducing sugars. Per cent.	Sugars. Cane-sugar added. Per cent.	Sugars. Cane-sugar found. Per cent.	Sugars. Added cane-sugar inverted. Per cent.	Polarization. Direct at 18° C.	Polarization. Invert at 18° C.	Polarization. Invert at 86° C.
20408	Apple (fall pippin)	59.18	0.22	0.279	0.175	20.78	51.76	33.04	36.17	+ 24.0	— 20.6	— 1.2
20405	Blackberry	59.63	0.33	0.475	0.243	12.51	54.89	44.90	18.20	+ 47.0	— 20.1	0.0
20410	Crab apple	63.28	0.11	0.171	0.137	34.93	57.61	23.68	58.88	+ 13.0	— 19.0	0.0
20405	Grape (Ives seedling)	63.66	0.45	0.524	0.175	32.29	60.29	30.52	49.33	+ 22.3	— 18.9	+ 0.2
20412	Huckleberry	63.02	0.28	0.245	0.069	24.27	53.39	32.74	37.54	+ 24.1	— 20.1	— 0.4
20435	Orange (Florida navel)	68.56	0.30	0.171	0.418	3.95	65.59	62.52	4.91	+ 61.3	— 23.1	— 0.2
20437	Peach	69.98	0.21	0.245	0.175	8.75	63.70	56.59	11.16	+ 53.4	— 23.0	— 0.6
20434	Pear (Bartlett)	69.12	0.34	0.181	0.156	6.58	63.09	58.46	7.33	+ 52.7	— 26.2	— 1.8
20436	Pineapple	80.28	0.43	0.328	0.387	22.13	72.98	56.70	28.45	+ 50.4	— 26.1	0.0
20433	Pineapple husk	76.34	0.73	0.352	0.350	7.40	70.22	65.22	7.12	+ 63.7	— 24.3	— 0.6
20404	Plum (Damson)	45.56	0.68	1.127	0.350	19.18	38.00	22.67	40.38	+ 17.8	— 12.8	0.0
20409	Plum (wild fox)	54.49	0.40	1.029	0.138	24.00	48.05	25.48	46.97	+ 16.7	— 17.8	0.0
20411	Plum (wild fox) boiled down	73.01	0.65	1.529	0.175	44.22	64.66	22.37	66.18	+ 7.6	— 22.6	— 0.6
20407	Mixed fruit	66.58	0.21	0.367	0.069	39.70	59.72	24.22	40.38	+ 14.8	— 17.9	+ 2.2

TABLE III.—FRUIT.[1]

Laboratory No.	Description of sample.	Total solids. Per cent.	Ash. Per cent.	Total acids calculated as H_2SO_4. Per cent.	Proteids (N × 6.25). Per cent.	Sugars. Reducing sugars. Per cent.	Sugars. Cane-sugar added. Per cent.	Sugars. Cane-sugar found. Per cent.	Sugars. Added cane-sugar inverted. Per cent.	Polarizations. Direct at 18° C.	Polarizations. Invert at 18° C.	Polarizations. Invert at 86° C.
20449	Apple (fall pippin).....	8.25	0.30	0.499	....	4.13	....	1.03	....	— 2.2	— 3.6	— 1.8
20415	Blackberry.....	9.62	0.60	0.916	0.725	5.67	....	....	....	— 1.1	— 1.0	0.0
20418	Crab apple.....	14.34	0.84	0.705	0.418	5.68	....	1.70	....	— 0.7	— 3.0	— 0.8
20417	Grape (Ives seedling)...	12.50	0.75	....	....	6.11	....	0.29	....	— 1.6	— 2.0	0.0
20425	Orange (Florida navel) .	13.11	0.61	0.686	0.985	4.13	....	3.33	....	+ 2.0	— 2.5	— 0.8
20444	Pineapple	13.71	0.50	0 392	0.056	8.12	....	3.11	....	+ 1.0	— 3.2	— 0.0

[1] The composition here given is not that of the original fruit, but of the pulped mass used in the preparation of jams.

TABLE IV.—JAM.

Laboratory No.	Description of sample.	Total solids. Per cent.	Ash. Per cent.	Total acids calculated as H_2SO_4. Per cent.	Proteids (N × 6.25). Per cent.	Sugars. Reducing sugars. Per cent.	Sugars. Cane-sugar added. Per cent.	Sugars. Cane-sugar found. Per cent.	Sugars. Added cane-sugar inverted. Per cent.	Polarizations. Direct at 18° C.	Polarizations. Invert at 18° C.	Polarizations. Invert at 86° C.
20446	Apple (fall pippin).....	63.22	0.20	0.282	0.175	25.52	51.31	29.11	43.22	+ 26.3	— 13.0	+ 4.8
20414	Blackberry	55.42	0.48	0.851	0.737	18.77	43.99	29.00	34.08	+ 24.6	— 14.6	+ 1.6
20419	Crab apple.....	41.82	0.27	0.715	0.493	14.80	36.09	23.04	35.46	+ 18.3	— 12.8	— 0.6
20445	Grape (fox)	61.80	0.19	0.698	0.200	50.06	54.21	3.70	92.96	— 9.0	— 14.0	+ 2.2
20416	Grape (Ives seedling)..	56.64	0.48	0.744	0 525	33.44	42.45	11.33	73.38	+ 3.5	— 11.8	0.0
20443	Orange (Florida navel).	80.52	0.44	0.433	0.944	13.61	69.13	54.23	21.55	+ 55.9	— 17.5	+ 2.0
20448	Pear (Bartlett).....	61.52	0.28	0.163	0.312	13.20	46.52	33.74	18.87	+ 32.3	— 13.2	+ 1.0
20442	Pineapple marmalade) .	73.92	0.30	0.315	0.312	14.05	60.20	46.40	22.90	+ 52.3	— 10.3	+ 6.2
20421	Plum (Damson).....	50.43	0.54	1.012	0.525	28.29	37.75	9.70	74.42	+ 3.1	— 10.0	+ 1.2
20423	Plum (wild fox).....	62.10	0.46	1.355	0.212	28.78	47.86	23.26	53.43	+ 13.9	— 17.5	0.0

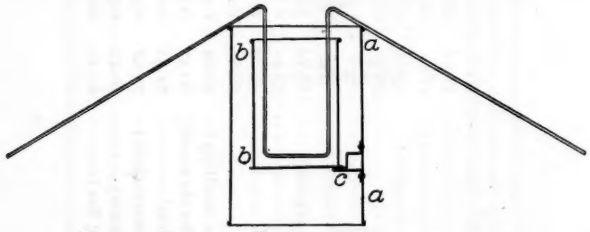
ON THE DETERMINATION OF HYDROGEN IN GAS MIXTURES.

By Francis C. Phillips.

Received March 11, 1901.

THE strongly exothermic character of the reaction involved in the combustion of hydrogen renders it possible to determine this gas by oxidation over palladium asbestos without the application of external heat. As the moisture produced in the reaction is liable to condense and cause the palladium to become wet, it is usual to apply heat in order to prevent this condensation and to insure the completeness of the reaction. For this purpose Winkler[1] recommends the use of a gas flame placed directly below the palladium asbestos tube. In heating over a flame the obvious danger occurs of burning hydrocarbons along with the hydrogen. The use of hot water as a source of heat presents the advantage that the temperature of the palladium is prevented from rising much above 100° C., provided that the rate of passage of the gas through the palladium asbestos tube is slow. Still it is somewhat difficult by any existing device to preserve a constant and definite temperature. The form of apparatus described below has proved convenient for maintaining the palladium asbestos at the temperature of boiling water for a period of time sufficient for the performance of a series of hydrogen determinations.

In the drawing, which represents the apparatus in section, *a a*



is a brass cylinder 30 cm. long and 18 cm. wide. It is open at both ends, the rims being strengthened by wires. *b b* is a cup-shaped vessel 18 cc. deep and 12 cc. wide. When in use this inner vessel rests upon three supports which are riveted to the

[1] Winkler and Lunge: "Handbuch of Technical Gas Analysis," 1885, p. 79.

inner surface of the cylinder *a a*. One of these supports is shown at *c*. The space between the cup and the cylinder is nearly 3 cm. wide. The cup is silvered on the outside and the cylinder is silvered on both sides. Any of the mixtures which are sold for giving a silver coating to brass will serve for the purpose.[1] The palladium asbestos is introduced into the middle of a glass tube 70 cm. long and about 3 mm. in internal diameter. The tube is then bent into the form shown in the sketch and the U-shaped part placed in the brass cup, which is then filled with water. A small flame is kept burning under the cup and the water maintained at a temperature approaching the boiling-point. The glass tube containing the palladium asbestos is connected at one end with a gas burette and at the other end with a Hempel pipette. The gas in which the hydrogen is to be determined, together with the necessary volume of air having been introduced into the burette, and the water-levels being carefully adjusted, the gas is caused to flow slowly through the palladium asbestos tube into the pipette, and back again to the burette, the volume of the hydrogen being ascertained in the usual manner. The polished silver surfaces prevent radiation to such an extent that the accuracy of the gas measurements is not affected by the close proximity of the measuring apparatus to the source of heat.

The palladium asbestos is prepared by moistening long-fibered asbestos with palladium chloride solution and igniting over a Bunsen burner flame, the process being repeated until the asbestos receives a sufficient quantity of the reduced metal (about 6 per cent. of the weight of the original asbestos has been found to be a convenient proportion). The deposition of the palladium occurs mainly on the surface of the bundle of asbestos fibers. It is well, therefore, in order to distribute the reduced metal as evenly as possible throughout the mass of the asbestos, to roll the fibers under a glass rod on a glass plate once or twice during the process of alternately impregnating with palladium chloride and igniting. Minute crusts of palladium accumulated upon the surface of the asbestos are liable to glow intensely, even when the

[1] A silvering mixture may be prepared according to the following formula: Dissolve 8 grams of silver nitrate, 10 grams of potassium cyanide, and 0.5 gram of potassium tartrate in 100 cc. of water. Add sufficient French chalk to make a thin paste. This mixture, applied with friction by help of a piece of Canton flannel, will produce a highly lustrous silver surface upon brass or copper.

tube is immersed in water, during the passage of a gas containing hydrogen and oxygen, and by so doing cause a partial combustion of any hydrocarbons that may be present. It is important, therefore, that the palladium should be distributed as uniformly as possible throughout the asbestos. As a result of the ignition, after impregnation with palladium chloride solution, the asbestos becomes somewhat more rigid and the bundle of fibers may be readily pushed, by help of a copper wire, far into the narrow glass tube.

[CONTRIBUTION FROM THE SHEFFIELD LABORATORY OF YALE UNIVERSITY.]

ON THE SEPARATION OF TUNGSTIC AND SILICIC ACIDS.

BY H. L. WELLS AND F. J. METZGER.

Received April 15, 1901.

IN a recent number of a German periodical[1] appears an article by Otto Herting, of Philadelphia, in which the assertion is made that the method given in the text-books for expelling silica from tungstic acid by means of hydrofluoric acid is incorrect. This statement is made on the ground of alleged numerous quantitative experiments with mixtures of pure tungstic acid and pure ignited silicic acid, but no details in regard to the results are given. Herting believes that upon ignition, silicic and tungstic acids form a silicotungstic acid which is volatile when treated with hydrofluoric acid, and finally says that he should be pleased if, by means of his article, he should bring about the more careful study of the "action of hydrofluoric acid upon tungstic acid in the presence of silicic acid."

Since Herting's statement throws doubt upon a method that is generally used, we have undertaken an examination of the matter. For this purpose, we dissolved some of Kahlbaum's tungstic acid in ammonia, precipitated with nitric acid, washed with water by decantation, digested repeatedly with sulphuric acid of sp. gr. 1.378 to separate any molybdic acid that might possibly be present,[2] washed the residue and ignited it. The tungstic acid thus prepared was used for the experiments that follow.

A weighed quantity of tungstic acid in a platinum crucible

[1] *Ztschr. angew Chem.*, 1901, 165.

[2] See Ruegenberger and Smith : This Journal, **22**, 772.

was mixed with about an equal quantity of pure silica. The mixture was covered with dilute sulphuric acid, a liberal amount of pure hydrofluoric acid added, the liquid carefully evaporated, and the residue ignited over a Bunsen burner. Then another portion of silica was added and the operation repeated. The results are shown in the following table:

	Taken.		Tungsten trioxide found after	
	Tungsten trioxide. Gram.	Silica. Gram.	First operation. Gram.	Second operation. Gram.
I.	0.1928	0.2	0.1927	0.1928
II.	0.2097	0.2	0.2097	0.2096
III.	0.2100	0.2	0.2099	0.2100
IV.	0.1999	0.2	0.2000	0.1998

The greatest error found in these experiments is 0.0001 gram and they show that the process is perfectly exact under these conditions.

Other experiments showed that long ignition of the mixed tungstic and silicic acids over the Bunsen burner before expelling the silicic acid had absolutely no effect upon the results. It was thought that in the absence of sulphuric acid a loss might occur by the treatment of tungstic acid with hydrofluoric acid, and the following experiments were made to test this point, no sulphuric acid being used:

Taken.		
Tungsten trioxide. Gram.	Silica. Gram.	Tungsten trioxide found. Gram.
0.1983	0.2	0.1983
0.2102	0.2	0.2100
0.2106	0.2	0.2105
0.1996	0.2	0.1994

In these experiments, the greatest error, 0.0002 gram, is well within reasonable limits; hence, it is evident that the absence of sulphuric acid has no effect. It is to be noticed that in these cases also, the tungstic acid was ignited by the Bunsen flame only.

Attention should be called to the fact that tungstic acid must not be ignited by means of the blast-lamp, since at the temperature thus produced, it volatilizes to a considerable extent. The books of reference do not give proper warning in regard to this matter. The following table gives the results of a series of experiments made by heating some of the substance (which showed no loss of weight over the Bunsen burner) over the blast-lamp in a platinum crucible:

	Weight of tungsten trioxide. Gram.	Loss. Gram.
Taken	0.3007	.....
Ignited for two minutes	0.2978	0.0029
" " " " again	0.2962	0.0016
" " " " "	0.2946	0.0016
" " " " "	0.2932	0.0014
" " " " "	0.2924	0.0008
" " " " "	0.2916	0.0008
" " " " "	0.2906	0.0010
" " five " "	0.2872	0.0034
	Total loss....	0.0135

All the ignitions except the last were made with a lamp provided with a water-blast, which gave a flame of only moderate power. The last ignition was made with a lamp connected with a foot bellows, which gave a considerably higher temperature. It is noticeable that the losses show a tendency to diminish after the first ignition, but this is probably due to a change in the physical condition of the oxide rather than to the removal of some more volatile substance. It is hardly possible that our carefully purified tungstic acid, which showed no loss when heated with a good Bunsen burner, could contain an amount of molybdic acid or other volatile substance sufficient to give the results that have been obtained. The loss shown in the table above amounts to nearly $\frac{1}{2}$ per cent., while inan other experiment 0.1955 gram of tungstic acid lost over 7 per cent. after heating with the blast-lamp for twenty minutes. It should be stated that the platinum crucible in which these ignitions were made showed no loss in weight after it had been cleaned.

We have shown that Herting's criticism of the usual method for separating silicic and tungstic acids is without foundation, and it appears probable that his difficulties were due to igniting tungstic acid at a too elevated temperature.

SHEFFIELD SCIENTIFIC SCHOOL,
April, 1901.

POTASSIUM PERSELENATE[1]—PRELIMINARY NOTE.

BY L. M. DENNIS AND O. W. BROWN.
Received April 2, 1901.

POTASSIUM perselenate was prepared by the electrolysis of a saturated solution of potassium selenate containing a little free selenic acid. This solution was placed in a 150 cc.

[1] The experimental work herein described was performed by Mr. Brown in the spring of 1898. It has been impossible to resume the work until recently, but it is hoped that the investigation may soon be carried to completion.

beaker and the anode, a platinum plate of about 15 sq. cm. surface, was introduced into it. The cathode, a piece of platinum foil, was contained in a small porous cup of about 75 cc. capacity which was suspended in the solution. This porous cup was filled with a dilute solution of selenic acid. The beaker was placed in a freezing-mixture and a current varying from 2.5 to 3 amperes was passed through the solution. The temperature in the outer cell averaged about 4° C.

After the action of the current had continued for some hours, a white substance began to appear in the neighborhood of the anode, its formation being accompanied by an increase in the resistance of the cell. After considerable of the solid had separated, the process was interrupted, the solution in the beaker was decanted, and the substance dried on a porous plate. It was then placed in a desiccator containing phosphorus pentoxide, and this was placed upon ice.

The complete analysis of the substance was not made at the time but merely the available oxygen was determined, this being done, first by adding oxalic acid in excess and determining the excess by means of potassium permanganate, and second, by adding ammonium ferrous sulphate in excess and titrating this excess in the same manner.

The two methods gave agreeing results, for when used on a sample of potassium selenate containing a small amount of perselenate, oxalic acid and potassium permanganate showed 2.41 per cent. of $KSeO_4$, while the ammonium ferrous sulphate method gave 2.42 per cent.

Potassium perselenate was not obtained free from selenate, the highest percentage of perselenate in the product being 74.44.

Potassium perselenate, when hot, oxidizes manganese dioxide to potassium permanganate, quickly oxidizes ferrous sulphate in the cold, and acts similarly upon thallous sulphate. An aqueous solution of the salt gives off oxygen when warmed.

CORNELL UNIVERSITY,
April, 1901.

NOTES.

On Methods of Sugar Analysis.—In the March number of the Journal of the American Chemical Society there is published a paper by Professor H. W. Wiley on "The Fourth International

Congress of Applied Chemistry," which, it appears, was read before the Northeastern Section of the American Chemical Society, January 17, 1901.

In that article (on page 188) Professor Wiley refers to some of the topics which engaged the attention of the "International Committee on Unification of Methods of Sugar Analysis."

Professor Wiley writes: "In the meeting of this committee, the data relating to the influence of temperature on polarizations were presented at length by M. Wiley of the United States, and M. Brodhun, of Germany. The only advocate of the stability of specific rotation, independent of temperature, was M. Wiechmann of the United States. The opinions of the majority were embodied in a resolution which finally passed the International Committee without a dissenting vote. This resolution was to the effect"...(For wording of this resolution, see this Journal, Vol. 23, page 62). Professor Wiley continues: "The influence of temperature on specific rotation has now been so thoroughly worked out that we may say without hesitation that the points established by Andrews eleven years ago, are now fully accepted by practically all the investigators of the world."

These statements tend to give to one not familiar with the facts, the impression that the majority of the members present indorsed the opinion, that the specific rotatory power of sucrose is affected by changes in temperature.

As a matter of fact the International Committee studiously avoided any expression of opinion on this question which had been a prominent topic of discussion between Professor Wiley and myself that day, before this body.

It was for this very reason that Professor Wiley's resolution, that his method of correcting polarization readings for the influence of temperature be adopted, was not accepted by the committee. Instead of this, the resolution offered by Mr. Sachs and cited above, was unanimously adopted.

An amendment which, Professor Wiley suggested, Mr. Sachs should include in his resolution, and which amendment would practically have allowed the use of Professor Wiley's method of temperature correction as an alternate method, was declined by Mr. Sachs.

This International Committee, which numbers among its members some of the most eminent sugar chemists of Europe, there-

fore certainly did *not* endorse Professor Wiley's method of correction factors, which takes into account an alleged influence of temperature on the specific rotation of sucrose.

This fact alone would seem to cast serious doubt on the validity of the opinion hazarded, "without hesitation," by Professor Wiley, "that the points established by Andrews eleven years ago, are now fully accepted by practically all the investigators of the world."

F. G. WIECHMANN,
Secretary, The International Committee, etc.

APRIL 22, 1901.

BOOKS RECEIVED.

The Chemical Analysis of Iron. A complete account of all the best known methods for the analysis of iron, steel, pig-iron, iron ore, limestone, slag, clay, sand, coal, coke, and furnace and producer gases. By Andrew Alexander Blair. Fourth Edition. Philadelphia: J. B. Lippincott Co. 1901. 319 pp. Price, $4.00.

A Compendium of Gold Metallurgy and Digest of U. S. Mining Laws, Water Rights and Desert Land Laws, by E. M. and M. L. Wade, 115½ North Main St., Los Angeles, Cal. 140 pp.

Condimental and Medicinal Cattle and Poultry Foods, Bulletin 132. February, 1901. Connecticut Agricultural Experiment Stations, New Haven, Conn. 7 pp.

Spraying. Bulletin No. 70. November, 1900. 32 pp. Poultry Experiments. Bulletin No. 71. December, 1900. 20 pp. Commercial Fertilizers. Bulletin No. 72. January 1, 1901. 32 pp. West Virginia University Agricultural Experiment Station, Morgantown, W. Va.

The Sunflower Plant: Its Cultivation, Composition, and Uses. By Harvey W. Wiley. Bulletin No. 60, U. S. Department of Agriculture, Division of Chemistry, Washington, D. C. 32 pp.

Pure-food Laws of European Countries, affecting American Exports. Prepared, under the direction of H. W. Wiley, by W. D. Bigelow. Bulletin No. 61, U. S. Department of Agriculture, Washington, D. C. 39 pp.

Experiments on the Effect of Muscular Work upon the Digestibility of Food and the Metabolism of Nitrogen, conducted at the University of Tennessee, 1897 to 1899. By Chas. E. Wait. Bulletin No. 89, U. S. Department of Agriculture, Office of Experiment Stations, Washington, D. C. 77 pp.

First Report on Food Products, for 1900. December, 1900. 61 pp. Fertilizer Analyses and Analyses of Iron Ores. January, 1901. 32 pp. Analyses of Fertilizers. February, 1901. 24 pp. North Carolina State Board of Agriculture, Raleigh, N. C.

Report of the Connecticut Agricultural Experiment Station for the Year

ending October 31, 1900. Part II. Food Products. Connecticut Agricultural Experiment Station, New Haven, Conn. 218 pp.

Milk, 1900. Bulletin No. 74, Laboratory of the Inland Revenue Department, Ottawa, Canada. 13 pp.

An Ephemeris of Materia Medica, Pharmacy, Therapeutics, and Collateral Information. Vol. VI, No. 3. January, 1901. Brooklyn, N. Y. 136 pp.

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A Manual of Laboratory Physics. By H. M. Tory, M.A., and F. M. Pritcher, M.Sc. New York: John Wiley & Sons. 1901. ix + 288 pages. Cloth, $2.00.

The Soy Bean as a Forage and Seed Crop. By C. S. Phelps. Bulletin No. 22, Storrs Agricultural Experiment Station, Storrs, Conn. 20 pp.

Experiments arranged for Students in General Chemistry. By Edgar F. Smith and Harry F. Keller. Fourth Edition, enlarged, with 41 illustrations. Philadelphia: P. Blakiston's Son & Co. 1900. 88 pp. Price, 60 c.

The American Year-Book of Medicine and Surgery, being a yearly digest of scientific progress and authoritative opinion in all branches of medicine and surgery, drawn from journals, monographs, and text-books, of the leading American and foreign authors and investigators. Under the general editorial charge of George M. Gould, M.D. Vol. I, Medicine. Philadelphia and London: W. B. Saunders & Co. 1901. 681 pp. Cloth, $3.00. Half morocco, $3.75.